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Chemical and physical characterisation of welding fume particles for distinguishing from gunshot residue

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ABSTRACT

Spherical particles produced by firearms loaded with a traditional ammunition reveal characteristic elemental contents and so their identification may provide a significant evidence in criminal investigations. With the advent of modern technologies in manufacturing ammunition, which replace toxic compounds of lead, antimony and barium in the primer mixture by elements and compounds such as powdered aluminium, titanium, amorphous boron or calcium silicide, differentiation between gunshot residue and morphologically similar particles originating from other anthropogenic or natural sources becomes more difficult. This work provides a chemical and morphological characterisation of welding fume particles originating from both the core and the covering of electrodes used in popular manners of welding steel and aluminium alloy constructions. With the use of scanning electron microscopy and energy dispersive X-ray spectrometry it has been established that single spherules containing aluminium, titanium or a set of such elements as aluminium, silicon, potassium and calcium may occur in result of welding processes, however, they are accompanied by great numbers of iron and iron oxide spherules. Thus, with this analytical method a population of welding particles can be distinguished from a population of gunshot residue originating from a modern type of ammunition, but a special care has to be taken when assessing the evidential value of single or few spherules consisting from light elements being detected in result of the search for gunshot residue for forensic purposes.

1. Introduction

When a firearm is discharged, the subsequent explosions of the primer and the propellant of a cartridge produce a heterogeneous population of gases, vapours and particles of varying chemical composition, called gunshot residue (GSR). Solid particles may contain not fully consumed material of the propellant or metals present in the compounds of the primer mixture, such as lead, antimony and barium associated with traditional type of ammunition, often recombined with other elements from the cartridge case, e.g. copper, zinc, nickel and tin, and from the barrel (iron, chromium and other elements left during previous shots) as well as the products of the propellant combustion and partially burned or just unburned grains of propellant. They adhere to obstacles on their way, including the shooter's hands, face and clothing, suspend in the atmosphere and finally deposit on various substrates in the close environment of the place, where the gun was fired [1,2].

Metallic particles originating from the traditional primer mixtures reveal both rare chemical combination of lead, antimony and barium as well as characteristic morphological properties resembling fast cooling of fine droplets of molten matter. That makes them distinguishable from other anthropogenic particulate matter by means of the scanning electron microscopy coupled with the energy dispersive X-ray spectrometry (SEM–EDX) [3]. The analytical approach based on SEM–EDX gained widespread success in various fields of science, mainly because the technique simultaneously provides the information on the elemental contents and morphological features of the materials of interest, and may focus on fine objects, e.g. particles of sizes in the range between sub-microns and dozens of microns.

Examinations of GSR can contribute to explaining of various aspects of a shooting incident, among which relating an individual with the use of firearm is the one of the greatest interest for forensic experts and practitioners of justice. The interpretation of the analytical findings for this purpose requires, among others, the

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knowledge on the dependence of the chemical content of GSR revealed at the crime scene on the type of ammunition used [4–10], on their distribution in the surroundings of the shooting gun [2,11–13], on the prevalence of GSR in general population and the persistence of the particles on the shooting person [14–19] as well as the consideration of alternative sources of particles similar to GSR. In the case of ammunition primed typically with the mixture of lead styphnate or lead azide as the detonator, barium nitrate – the oxidiser and antimony trisulfide as the fuel, one should take into consideration particles that may alternatively originate, e.g. from lighter flint, fireworks or car brake pads. Literature in this subject has demonstrated that the risk of mistaking particles from these sources for GSR remains low [20–22].

Nowadays ammunition manufacturing gradually changes towards replacing the heavy metal components of the primer with less toxic organic and inorganic compounds. In *sintox* type ammunition zinc peroxide acts as an oxidiser, powdered titanium as a fuel, diazo-dinitrophenol and tetrazene as the explosive and the sensitiser, respectively. In *nontox* ammunition by Sellier & Bellot, Vlasim, Czech Republic amorphous boron plays the role of fuel, potassium nitrate – an oxidiser and powdered glass as a frictionator. Gunshot particles originating from these kinds of modern ammunition consist of elements being abundant in the environment and so may cause difficulties in the interpretation and evaluation of the analytical findings. Their evidential value may be increased, when the comparative material originating from the interior of cartridge cases is available for examinations. However, in cases, when no comparative material can be obtained the identification of the particles to be GSR becomes a challenge for forensic experts again. Thus, there occurs an urgent need of a new and broadened critical study of the presence of similar spherules in the environment and whether they can be differentiated from GSR of the same elemental content by means of SEM–EDX technique.

One of the potential sources of particles occurring as a result of melting and fast cooling of metals can be welding, which is a popular manner of assembling metal objects in many types of constructions [23,24]. Welding is being applied not only in the industrial environments but also in modern building or mechanical workshops both professional and amateur. There are various welding techniques requiring different types of electrodes, e.g. very popular for mending and repairs method of shielded metal arc welding (SMAW), called also manual metal arc welding (MMA) requires a consumable shielded electrode, i.e. an electrode with a covering. Electric arc may generate temperatures of 3000–30,000 °C, in which the covering decomposes and produces airborne gases and slag blanket that protects the hot weld metal from the atmosphere as it cools. Electrode coatings can consist of a number of different compounds, e.g. rutile, fluorides, dolomite, kaolinite, cellulose and iron powder, which play certain roles in the process. Rutile electrodes, coated with 25–45% of TiO_2, are characterised by ease of use and good properties of the resulting weld. Both the metal core and the covering of the electrode contribute to welding fume being formed, when the elements and compounds are heated above their boiling points and then condensate from vapours to fine solid particulates, containing, e.g. aluminium or titanium that, on the other hand, can be present in the modern types of primers.

The aim of the presented work was a chemical and morphological study of particles originating from welding processes of steel and aluminium constructions that were collected from the welders' gloves to be compared with GSR particles originating from lead-less ammunition types.

2. Materials and methods

2.1. Selection of particles sources

The subject of the study were samples of the coverings of 10 electrodes of rutile, rutile–cellulose, alloy and alkaline types (Table 1) as well as samples of microtraces collected from the welders' gloves after welding either steel or aluminium constructions. Nine electrodes were related to welding of steel elements and one of them to welding of aluminium alloys. A pair of brand new leather gloves was used for each experiment. Selected populations of titanium particles originating from *sintox* ammunition (Dynamit Nobel, Troisdorf, Germany) and aluminium particles originating from two other types of ammunition (Cartridges Saga, Lleida, Spain and Mesko Metal Works, Skarżysko-Kamienna, Poland) were included in the study for comparison.

2.2. Specimen collection and preparation

Aluminium stubs with adhesive carbon tabs by TAAB Laboratories Equipment Ltd., Berks, UK, were used. Samples of the

Table 1
Welding electrodes used to obtain specimens of welding fume particles.

Rutile electrodes		
1.	ER 246 AWS E 6012	Thick-coated with rutile coating general-purpose electrode (C, Si, Mn) for welding of steel constructions
2.	ER 346 AWS E 6012	statically and dynamically loaded (ship constructions, containers and pipelines, etc.).
3.	FOX CN 23/12-A 17E	Stainless steel electrode (C = 0.02, Si = 0.7, Mn = 0.7, Cr = 23.0, Ni = 12.5) with a rutile coating.
Alkaline electrodes		
4.	EVB 50 P/E 7018	Basic coated electrode for welding of constructions of steel and other materials with higher resistance, e.g. shipyard industry, machine-building, rail-way construction with dynamic load, welding with direct or alternating current in various positions.
5.	EB 150/E 7018	
6.	EBS	Electrode for welding low-alloy steels and low-carbon steels, producing crack-free welded joints with good toughness properties.
Rutile-cellulose electrode		
7.	RUT WELD 12	Medium-coated general-purpose electrode (C, Si, Mn) for assembling of low-carbon steel constructions.
Special electrodes		
8.	316L-17/SKR AC/DC	High capacity electrode for welding high-alloyed steels of grades 316L (Mo = 3.0, Ni = 8.0, Cr = 18.0), rutile coating, welding with direct or alternating current.
9.	83503ELGA308E/E308L 17	High capacity electrode for welding stainless steels of grade 308L (C < 0.04, Si = 0.9, Mn = 0.7, Cr = 19.0, Ni = 9.5), rutile coating.
Alloy electrode		
10.	AlSi5 OK 9640	Electrode for repairing castings made of aluminium alloys (Mn < 0.5, Fe < 0.5, Si = 5.0).