

Elemental analysis of primer mixtures and gunshot residues from handgun cartridges commonly encountered in Taiwan

Hsien-Hui Meng,^{1,*} Ph. D.; Hsei-Chang Lee,^{1,2} M. Sc.

¹ Department of Forensic Science, Central Police University, 56 Shu Jen Road, Taoyuan 33304, Taiwan, ROC

² Firearms Section, Forensic Science Center, Criminal Investigation Bureau, National Police Administration, Taiwan, ROC

Received: April 30, 2007 / Received in revised form: July 18, 2007 / Accepted: July 18, 2007

Abstract

Inorganic gunshot residues (GSR) can arise from each component of the fired cartridge and GSR deposits inside the barrel from previous shootings. This work focused on the analysis of primer mixtures that yield GSR-unique particles. Primer mixtures and gunshot residues from 25 kinds of cartridges were recovered and subjected to scanning electron microscopy/energy dispersive X-ray analysis to obtain morphological and compositional data. The results revealed that 17 kinds of cartridges using non-corrosive primer that contained lead styphnate, barium nitrate, and antimony sulfide. The identity of lead styphnate was confirmed by its distinctively shaped rhombic crystals. In addition to Pb, Sb, Ba, and S, other elements such as Al, Ca, Si, and P were also detected in non-corrosive primers. Seven kinds of cartridges were found to use lead-free primers, where two of them contained Sb, Ba, and S. Major elements detected in the other lead-free primers were common elements such as K, Mg, and Zn except that strontium was detected in one primer and zirconium was detected in another.

Major elements detected in GSR particles were generally in accordance with those of their respective primers. Other minor elements from various sources were also detected. The Pb-Sb-Ba unique particles were detected in all GSR samples from cartridges using non-corrosive primer with the exception of S&B 9 mm cartridge where Pb-Ba-Sn particles were detected. The elements detected in particles from lead-free cartridges were not as characteristic as typical GSR except that Sb-Ba were detected in GSR from two lead-free cartridges. The Sb-Ba particles were regarded as GSR specific when their spherical morphology was simultaneously taken into account. Gunshot residue particles from gun hands and targets were mainly spheroidal in shape with a diameter smaller than 10 μm . Gunshot residues from spent cases were usually irregular in shape and present as flakes or aggregated mass sometimes bigger than 100 μm . The elemental composition of GSR was found to be primer type dependent. To reach a meaningful interpretation of GSR analysis results, the comparison of suspected GSR particles with known GSR of the cartridge used is even more important than the uniqueness of the particles' elemental composition. Gunshot residues recovered from the spent case, the fired bullet, and the bullet hole could be used for comparison. If the firearm and the cartridge used in the crime are available, primer mixtures and GSR from test firings should also be analyzed.

Keywords: forensic sciences, firearms examination, gunshot residues, primer mixtures, scanning electron microscopy / energy dispersive X-ray spectrometry (SEM/EDS)

Introduction

When a gun is discharged, a mixture of vapors and particulate material are expelled from the muzzle, ejecting port, barrel/cylinder gap or open breech. These products of firearm discharge are collectively called gunshot residues (GSR). Features of GSR have been used to estimate the range of firing [1,2,3,4,5], to identify

bullet holes [1,6,7,8], and most importantly, to determine whether or not a person has contacted a surface exposed to GSR (firearms, spent cartridge cases, entrance holes) and/or has been in the vicinity of a shooting incident [9,10,11,12,13,14]. The unique elemental composition and characteristic spherical shape of GSR are usually identified using scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) which

*Corresponding author, E-Mail: una106@mail.cpu.edu.tw

allows the identification of a single GSR particle in non-destructive way and gives a high selectivity unparalleled by any bulk analysis methods. Inorganic GSR can arise from the primer mixtures, the bullet, the cartridge case, the propellant powder, and GSR deposited inside the barrel from previous discharge of cartridges [15]. A work on the elemental analysis of bullets commonly encountered in Taiwan has been published by this author [16]. GSR originating from primer is unique to the discharge of firearms because of their characteristic elemental composition of lead, antimony, and barium [17]. Thus, the elemental analysis of primer mixtures of commonly encountered handgun cartridges would be practically useful for the detection of GSR and investigation of shooting events [18].

According to the location of the primer, small-arms

cartridges are categorized as center-fire cartridges and rim-fire cartridges. There are three types of center-fire primers: Boxer, Berdan, and Battery Cup. The Battery Cup primers are exclusively used for shotgun cartridges. With the exception of cartridges manufactured in the present or former communist countries, which have Berdan primers, all cartridges encountered in Taiwan have Boxer primers. A Boxer primer consists of a metal primer cup, a pellet of primer mixtures, a paper disk and an anvil. The Boxer primer has a single flash hole in the center of the primer pocket. The Berdan primer differs from the Boxer primer in that the anvil is a projection from the center of the primer pocket rather than an integral component. Berdan primers have two flash holes beside the anvil. Fig 1 presents the differences between Boxer and Berdan primers.

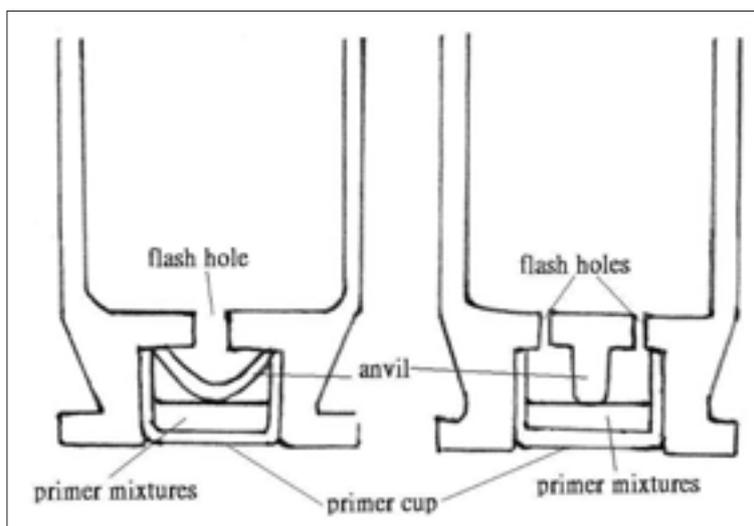


Fig. 1 The differences between Boxer (left) and Berdan (right) primers.

The primer mixtures consist of four basic chemical components: the initiating explosive, oxidizing agent, fuel, and sensitizer. Each component can contribute more or less ingredients to the GSR after a gun has been fired. Primer mixtures are classified as mercuric, chlorate, non-corrosive, and lead-free primers, depending on their chemical composition. The most popular primer composition at present is the non-corrosive primer. The initiating explosives are basically primary high explosives which are so sensitive as to explode when struck by the striker or firing pin of a weapon, starting a flame to ignite the propellant in a small-arms cartridge. The initiator in non-corrosive primers is lead styphnate

although formerly lead azide, potassium chlorate and mercury fulminate were used to serve as initiator in the primers. The latter three are no longer commonly used because of insufficient intensity of flame produced and a corrosive effect imparted to the gun barrels. Oxidizing agents are used in primers to increase the heat of ignition and barium nitrate is the most commonly used oxidant in small-arms ammunition, but barium peroxide, lead nitrate, or lead peroxide may also be used. Antimony sulfide is commonly used as fuel in primers, but calcium silicide, lead thiocyanate, powdered aluminum, and powdered zirconium, magnesium, and titanium have also been employed [19]. The standard sensitizer used

in small-arm primers is tetracene [1-(5-tetrazolyl)-4-guanyltetrazene hydrate] while pentaerythritol tetranitrate, trinitrotoluene, and tetryl are also used [19].

Although the analysis of GSR using SEM/EDS has been thoroughly studied, the analysis of primer mixtures of cartridges has seldom been reported [20]. Thus, not only GSR but also primer mixtures obtained from both collected cartridges and confiscated illegal cartridges were elementally analyzed in this work. The aim of this work is to obtain elemental composition data of primer mixtures of handgun cartridges frequently encountered in Taiwan and to provide procedures for identifying GSR originating from cartridges used in criminal activities through comparative analysis of GSR and primer mixtures of suspected cartridges.

Experimental

Instruments and materials

1. JSM-5410LV Scanning Electron Microscope (SEM), Jeol, Japan. Acceleration voltage: 20 KV. Tilt of sample: 0°. Working distance: 15 mm. Images observed: secondary electron images and backscattered electron images.
2. LINK ISIS energy dispersive X-ray analyzer, Oxford, UK. X-ray signals were collected from 0 to 20 KeV, 20 eV per channel. Peaks were either manually or automatically identified.
3. Firearms employed for test firings:
 - (1) Semiautomatic pistols: Glock 17 (9 mm Luger), S&W 4006 (.40 S&W), Hammerli 280 (.32 S&WL).
 - (2) Revolver: S&W MOD 649-2 (.38 Special).
4. Cartridges: Primer mixtures and/or GSR obtained

from 25 kinds of collected cartridges or confiscated illegal cartridges were analyzed. The details of these cartridge samples are shown in Table 1.

Methods

1. Analysis of primer mixtures: Bullets and propellants of unfired cartridges were removed employing inertia bullet extractor, the Boxer primer cups of unfired cartridge cases were deprimed, and primer mixtures were then recovered from the primer cups after removing the anvils. Primer mixtures were mounted on SEM sample stub using double-sided carbon tape. Mounted samples were carbon coated and subjected to SEM/EDS analysis.
2. Analysis of GSR: Cartridges were fired using firearms with appropriate calibers in an indoor shooting range toward white paper targets. GSR samples were collected from the web and back of the shooter's gun hand, the inside of the spent cartridge case, and the surface around the bullet hole after each test firing using a SEM sample stub attached with double-sided carbon tape. GSR samples were then carbon-coated prior to SEM/EDS analysis.

Results and discussion

Primer mixture analysis

Because the S&B 9 mm Luger cartridge has a Berdan type primer with two small eccentric flash holes (Fig. 1), the primer cup and primer mixture cannot be safely removed from the unfired cartridge case using the deprimer. Thus there was no primer mixture of this cartridge available for the EDS analysis. The major elements detected for the primer mixture collected from various cartridges except the S&B 9 mm Luger cartridge are shown in Table 2.

Table 1 Details of cartridge samples.

Caliber	Head Stamps	Sources	Samples analyzed
9 mm Luger	WCC 10-80	Confiscated	Primer mixtures
9 mm Luger	A-MERC	Confiscated	Primer mixtures
9 mm Luger	FC +P+	Confiscated	Primer mixtures
9 mm Luger	ACP 96	Confiscated	Primer mixtures
9 mm Luger	RP	Confiscated	Primer mixtures
9 mm Luger	SPEER	Confiscated	Primer mixtures
9 mm Luger	ACP 98	Confiscated	Primer mixtures
9 mm Luger	GFL(01) ^a	Confiscated	Primer mixtures
9 mm Luger	WIN(01) ^a	Confiscated	Primer mixtures
9 mm Luger	GFL(02) ^a	Collected	Primer mixtures & GSR
9 mm Luger	GFL(03) ^a	Collected	Primer mixtures & GSR
9 mm Luger	WIN(02) ^a	Collected	Primer mixtures & GSR
9 mm Luger	WIN(03) ^a	Collected	Primer mixtures & GSR
9 mm Luger	PMP	Collected	Primer mixtures & GSR
9 mm Luger	NPA 92	Collected	Primer mixtures & GSR
9 mm Luger	WRA	Collected	Primer mixtures & GSR
9 mm Luger	WP 92	Collected	Primer mixtures & GSR
9 mm Luger	S&B	Collected	GSR
.40 S&W	WIN	Collected	Primer mixtures & GSR
.38 SPL	WIN	Collected	Primer mixtures & GSR
.38 SPL	GECO	Collected	Primer mixtures & GSR
.38 SPL	GFL	Collected	Primer mixtures & GSR
.38 SPL	PMC	Collected	Primer mixtures & GSR
.32 S&WL	LAPUA	Collected	Primer mixtures & GSR
.32 S&WL	GECO	Collected	Primer mixtures & GSR

^a Different kinds of cartridges with the same head stamps.

Table 2 Elements detected in primer mixtures collected from various cartridges.

Cartridge	Elements detected	Cartridge	Elements detected
WCC 10-80, 9 mm	Pb, Sb, Ba, S, Al	WIN(03) ^a , 9 mm	K, Mg, Cu
A-MERC, 9 mm	Pb, Sb, Ba, S	WP 92, 9 mm	Pb, Sb, Ba, S, Al, Cu
FC +P+, 9 mm	Pb, Sb, Ba, S, Al	NPA 92, 9 mm	Pb, Sb, Ba, S, Al, Cu
ACP 96, 9 mm	Pb, Sb, Ba, S, Al	WRA, 9 mm	Pb, Sb, Ba, Al, Cu, P
ACP 98, 9 mm	Pb, Sb, Ba, S, Al	PMP, 9 mm	Sr
RP, 9 mm	Pb, Sb, Ba, S	WIN, .40 S&W	K, Mg, Zn, Cu
SPEER, 9 mm	Pb, Sb, Ba, S, Al	WIN, .38 SPL	K, Mg, Al
WIN(01) ^a , 9 mm	Pb, Sb, Ba, S, Al	GECO, .38 SPL	Pb, Sb, Ba, S, Si, Ca
GFL(01) ^a , 9 mm	Pb, Sb, Ba, S, Al	GFL, .38 SPL	Sb, Ba, S, Ca
GFL(02) ^a , 9 mm	Sb, Ba, S, Al, Cu, Si	PMC, .38 SPL	Pb, Sb, Ba, S, Al
GFL(03) ^a , 9 mm	Zr, K, Al, Si	LAPUA, .32 S&WL	Pb, Sb, Ba, S, Al
WIN(02) ^a , 9 mm	Pb, Sb, Ba, S	GECO, .32 S&WL	Pb, Sb, Ba, S, Si, Ca, Al

^a Different kinds of cartridges with the same head stamps

The results of primer mixture analysis revealed that 17 kinds of studied cartridges using non-corrosive primer contained lead styphnate as initiator, barium nitrate as oxidizer, and antimony sulfide as fuel. Elements Ba, Sb, Pb, and sulfur (S) were all detected in all of these non-corrosive primer mixtures. A typical EDS spectrum of Boxer type non-corrosive primer mixtures is shown in Fig.2. Due to the normally poor resolution of energy dispersive X-ray spectrum, the K lines of sulfur at the energy of 2.31 and 2.46 KeV were unresolved with the M lines of lead at 2.35 and 2.46 KeV. Thus S was not labeled on the spectrum. The identity of lead styphnate was confirmed by the observation of its distinctive rhombic crystals via secondary electron image. Fig. 3 illustrates the theoretical shape of the rhombic crystal of lead styphnate along with its SEM secondary electron images taken from three different angles. The EDS spectrum of a lead styphnate crystal with some aluminum fine particles attached to it is shown in Fig.4. Although the morphology of antimony sulfide and barium nitrate crystals is not as characteristic as that of lead styphnate,

the EDS spectra are useful for the identification of these crystals. The EDS spectrum indicating the presence of both S and Sb and, hence, the presence of antimony sulfide is shown in Fig. 5. The EDS spectrum of barium nitrate is shown in Fig. 6. In addition to these typical elements of non-corrosive primer mixtures, some other elements were also detected in some primer mixtures. Aluminum powder, a fuel usually used in small quantity along with other fuels [21], was detected in 14 samples. Through X-ray mapping analysis, it was found that Al existed as finely particles evenly distributed over the surface of other components. Ca and Si were detected in two samples (GECO, .38 SPL and GECO, .32 S&WL) indicating the presence of calcium silicide which is used as fuel. In the primer mixture of GFL(02) 9 mm and GFL(03) 9 mm cartridges, Si was detected without Ca indicating ground glass might have been used as frictionator. Phosphorous possibly originating from lead hypophosphite [22], a hardly used constituent in modern cartridge primers, was detected in the primer mixture of WRA 9 mm cartridge.

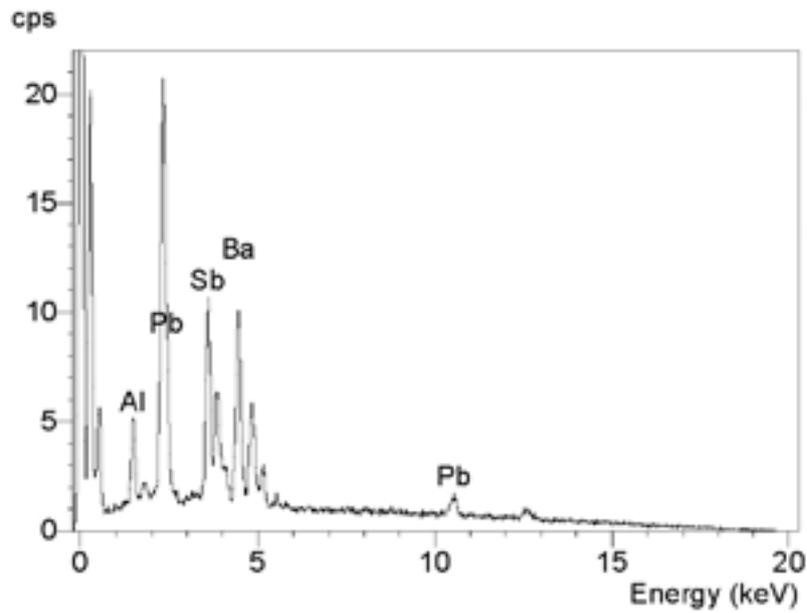


Fig. 2 A typical EDS spectrum of non-corrosive primer mixture.

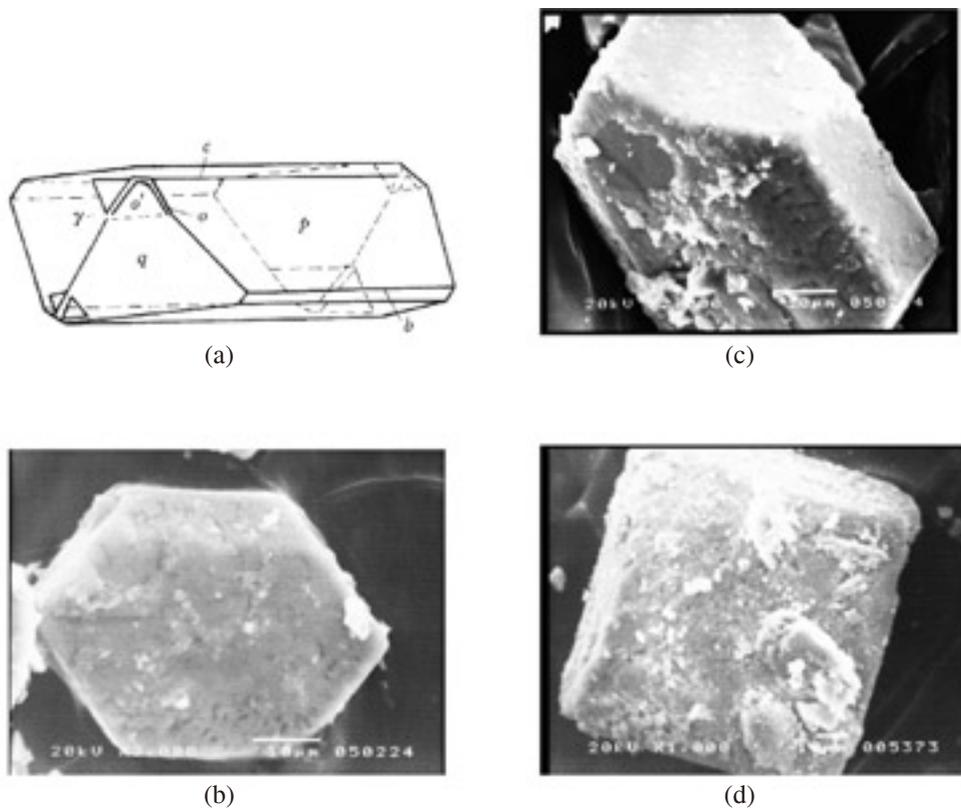


Fig. 3 The rhombic crystal of lead styphnate: (a) theoretical shape [23]; (b)-(d) SEM secondary electron images taken from three different angles.

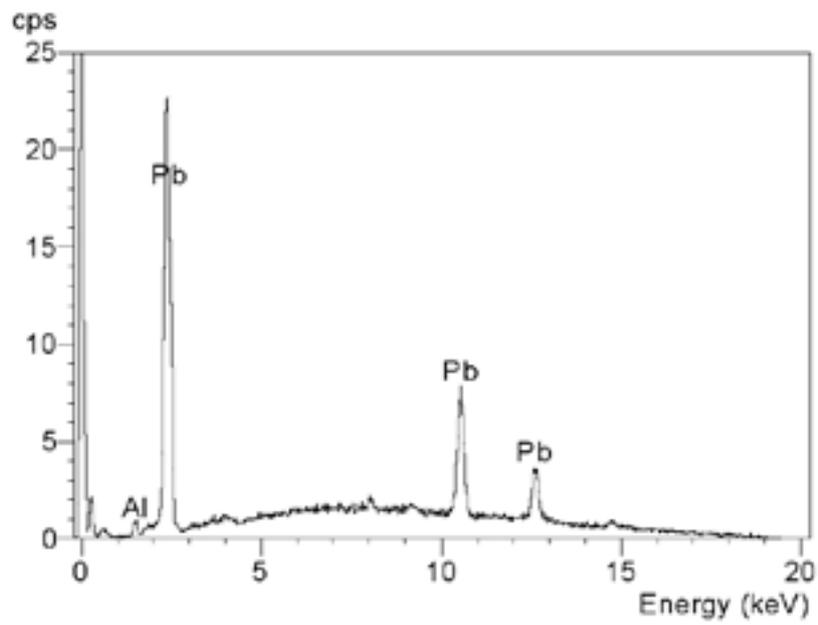


Fig. 4 The EDS spectrum of a lead styphnate crystal with aluminum fine particles attached to it.

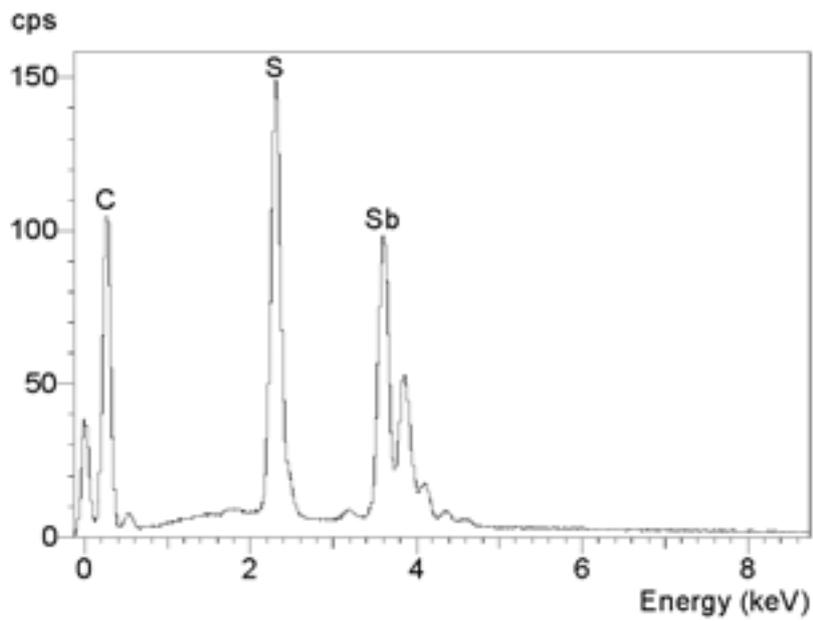


Fig. 5 The EDS spectrum of an antimony sulfide crystal.

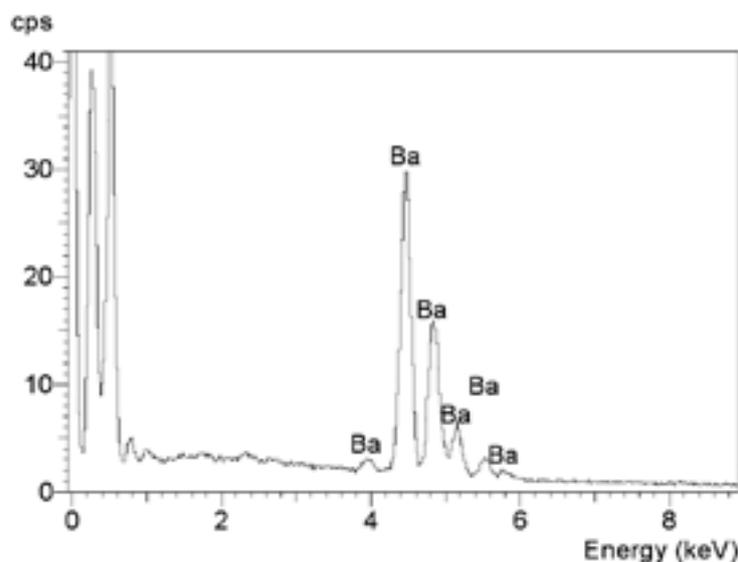


Fig. 6 The EDS spectrum of a barium nitrate crystal.

The GSR specific elements Pb, Sb, and Ba were detected in all primer mixtures recovered from confiscated cartridges. The results indicated that the lead-free cartridges are not yet popular on the domestic firearms black market. However, since the introduction of lead-free primer by the Dynamit Nobel AG in 1980, the use of lead-free cartridges to minimize airborne lead particles during discharging of firearms has become a trend all over the world. It is anticipated that the lead-free cartridges will be used by domestic criminals in the future. The subsequent diffusion of lead-free cartridges will cause problems for forensic scientists in the interpretation of GSR analysis results. Because the GSRs produced by lead-free cartridges are much less characteristic than those from non-corrosive primers, domestic forensic scientists should be aware of this phenomenon to avoid incorrect conclusions being made.

There are seven kinds of cartridges using lead-free primers, GFL(02) 9 mm, GFL(03) 9 mm, WIN(03) 9 mm, PMP 9 mm, WIN 40 S&W, WIN 38 SPL, and GFL 38 SPL, where lead turned out to be not detected. The most common substitute for lead styphnate in lead-free primer is diazodinitrophenol (DDNP) [24], an organic compound unidentifiable by SEM/EDS. Barium nitrate and antimony sulfide were also confirmed to be substituted by compounds without any heavy metals in four out of seven lead-free primers, namely GFL(03) 9 mm, WIN(03) 9 mm, WIN 40 S&W, and WIN 38 SPL. In other words, none of the traditionally characteristic elements such as Ba, Sb, and Pb were detected in these

heavy-metal-free primers. However, Sb and Ba were still detected in the primer mixtures of GFL(02) 9 mm and GFL 38 SPL. Strontium nitrate was used as a substitute for the conventionally used barium nitrate in the primer mixture of PMP 9 mm, as was detected in this sample [25]. The major elements detected in those heavy-metal-free primer mixtures were K, Mg, Zn, and/or Zr (zirconium). Zirconium is an unusual component which was detected only in one primer mixture, GFL(03) 9 mm (Fig. 7).

There are some 9 mm cartridges collected from various sources having identical head stamps indicating that they were made by the same manufacturer. However, our results revealed that their primer mixtures might have different elemental compositions; e.g., GFL(01) 9 mm, GFL(02) 9 mm, and GFL(03) 9 mm were all made by Fiocchi, Italy, but with different primer elemental compositions of (Pb, Sb, Ba, S, Al), (Sb, Ba, S, Al, Cu, Si), and (Zr, K, Al, Si), respectively. For primer mixtures from cartridges made by Winchester, USA, Pb, Sb, and Ba were detected in WIN(01) 9 mm and WIN(02) 9 mm, however only elements non-specific to GSR, such as K, Mg, and Cu, were detected in WIN03 9 mm. It is obvious that head stamps of spent cartridge case are useful for the identification of cartridge manufacturer and caliber, but is useless in predicting the possible elemental composition of primer mixture and GSR originating from the concerned cartridge. Thus a GSR sample recovered from the spent cartridge case should always be analyzed for comparative purpose while conducting GSR analysis.

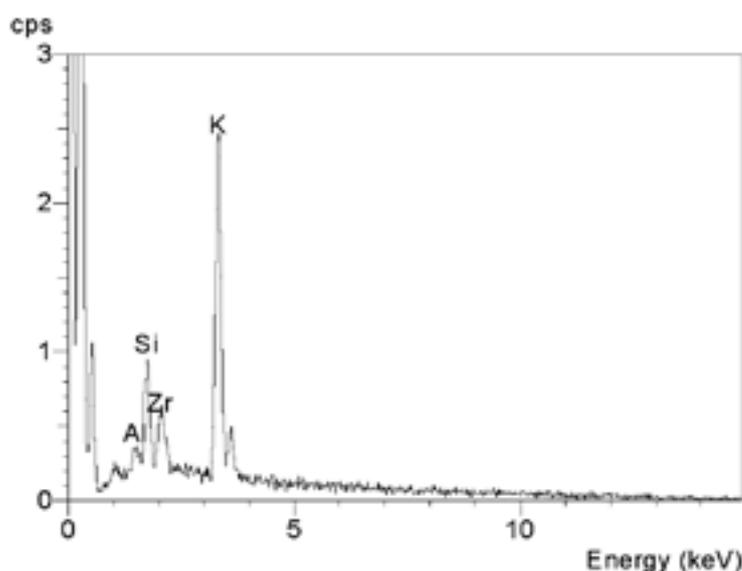


Fig. 7 The EDS spectrum of a lead-free primer mixture containing Zr.

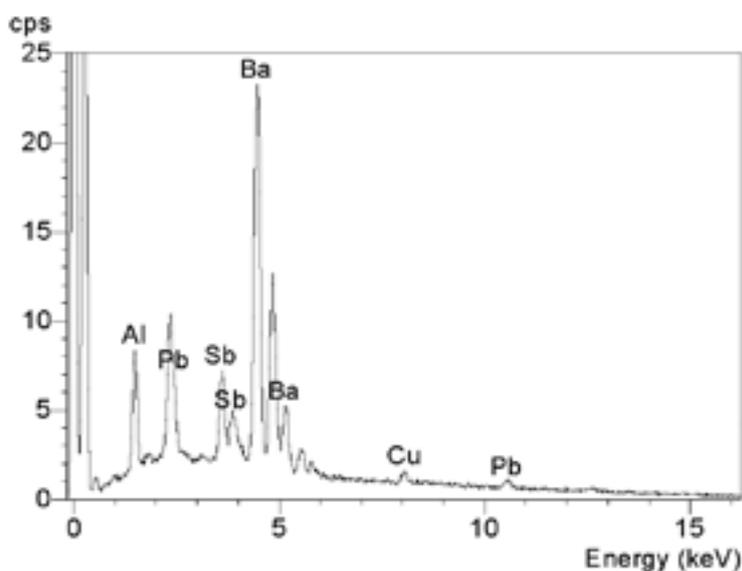
Gunshot residue analysis

The details of elements detected for the GSR samples from various test cartridges are shown in Table 3. Major elements detected in GSR samples collected from spent cartridge case, shooter's hand, and target surface after test-firing are generally in accordance with those detected in their corresponding primer mixtures. In addition to elements detected in primer mixtures, other minor elements were also detected in GSR samples. Extra elements detected in GSR from the spent case are attributed to the composition of cartridge case and propellant powder. Bullet materials, deposits inside the barrel, and materials on sampled surfaces might contribute additional elements to hand and/or target GSR samples. The so-called "tri-components unique

particles" containing Pb, Sb, and Ba were detected in all GSR samples generated by cartridges using non-corrosive primers with the exception of S&B 9 mm Luger cartridge. A typical EDS spectrum of a GSR particle containing Pb, Sb, and Ba is shown in Fig.8. Major elements detected in GSR samples from S&B cartridge were Pb, Ba, and Sn. Minor elements of Si, Ca, Cu, Zn, Fe, and Ni were also detected in S&B samples which were resulting from its unusual bullet composition and Berdan type primer [7, 12, 26]. The EDS spectrum of a GSR particle from S&B cartridge is shown in Fig.9. Elements of Cu, Zn, Fe, and Ni were contributed by its three-layered bullet jacket and coating [16]. The tin foil of Berdan type primer contributed Sn to GSR particles.

Table 3 Elements detected in GSR collected from targets, gun hands and spent cases.

Cartridge	Target GSR	Hand GSR	Case GSR
GFL(02) 9 mm	Sb, Ba, S, Al, Si, Ca, Fe, Cu, Zn	Sb, Ba, S, Al, Cu	Sb, Ba, S, Cu
GFL(03) 9 mm	Zr, K, Si, Al, Ca, Fe, S, Cu	Zr, K, Si, Al, Ca, S, Mg	Zr, K, Si, Ca, S, Cu, Zn
WIN(02) 9 mm	Pb, Sb, Ba, S, Si, Al, Ca, Fe, Cu, Ti	Pb, Sb, Ba, S, Si, Al, Ca, Fe, Cu, Zn, Cr	Pb, Sb, Ba, S, K, Cu, Zn
WIN(03) 9 mm	K, Fe, Si, Ca, Cu, Zn	K, Mg, Si, Ca, S, Cu	K, Fe, S, Cu, Zn
WP 92 9 mm	Pb, Sb, Ba, S, Al, Cu, Si, Ca	Pb, Sb, Ba, S, Al	Pb, Sb, Ba, S, Cu, Zn
NPA 92 9 mm	Pb, Sb, Ba, S, Al, Si, Ca	Pb, Sb, Ba, S, Al, Cu	Pb, Sb, Ba, S, Al, Cu
WRA 9 mm	Pb, Sb, Ba, S, P, Al, Cu, Si, Ca, Fe	Pb, Sb, Ba, S, P, Al, Cu	Pb, Sb, Ba, S, P, Cu
PMP 9 mm	Sr, Ti, Cu, Zn, Al	Sr, Ti, Cu, Zn	Sr, Ti, Cu, Zn
S&B 9 mm	Pb, Ba, Sn, Ni, Si, Ca, Fe, Cu, Zn, Al	Pb, Ba, Sn, Ni, Si, Ca, Fe, Zn, Mg, Cl, Al	Pb, Ba, Sn, Si, Ca, Cu, Fe, Al
PMC 38 SPL	Pb, Sb, Ba, S, Al, Si, Ca, Cu	Pb, Sb, Ba, S, Al	Pb, Sb, Ba, S, Al, Cu, Zn
GFL 38 SPL	Sb, Ba, S, Al, Si, Ca	Sb, Ba, S, Al, Si, Ca, Cu	Sb, Ba, S, Al, Si, Ca, Fe, Cu, Zn
WIN 38 SPL	K, Al, Si, Ca	K, Mg, Si, Ca, Fe, Cu	K, Al, Si, Cu, Zn
GECO 38 SPL	Pb, Sb, Ba, S, Cu	Pb, Sb, Ba, S, Si	Pb, Sb, Ba, S, Si, Cu, Zn
WIN 40 S&W	K, Mg, Cu, Si, Ca, S, Fe, Al, Ti	K, Mg, Si, Ca, S, Fe, Al	K, Cu, Zn, Si, Fe
GECO 32 S&WL	Pb, Sb, Ba, S, Si, Al, Ca, Cu	Pb, Sb, Ba, S, Si, Cu, Al	Pb, Sb, Ba, S, Si, Ca, Cu
LAPUA 32 S&WL	Pb, Sb, Ba, S, Si, Ca	Pb, Sb, Ba, S, Si, Cu, Ca	Pb, Sb, Ba, S, Al, Cu

**Fig. 8** EDS spectrum of a typical tri-components unique GSR particle.

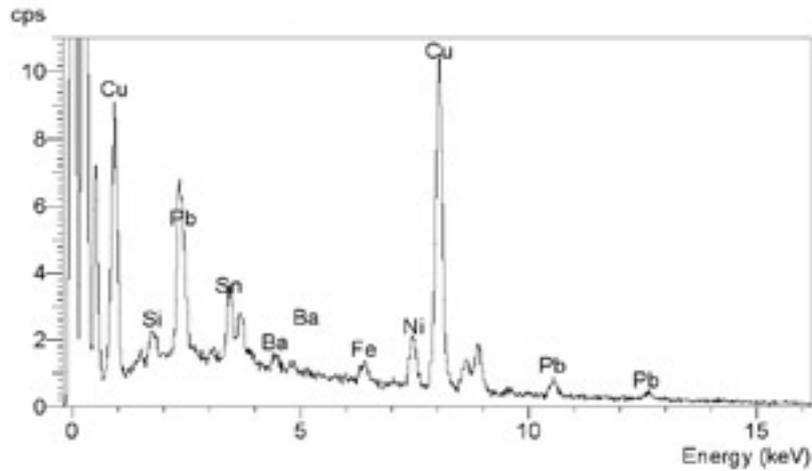


Fig. 9 The EDS spectrum of a GSR particle from S&B 9 mm cartridge.

In addition to Pb, Sb, and Ba, non-specific elements such as Al, Ca, Cl, Cu, Fe, K, Mg, P, S, Si, Ti, and Zn were also frequently detected in hand and target GSR samples from non-corrosive primer cartridges. The EDS spectrum of a GSR particle containing both GSR-specific and non-GSR-specific elements is shown in Fig.10. Al, Ca, P, S, and Si might come from primer mixtures as mentioned above; however, some of these additional elements might originate from other sources rather than primer mixtures. Al, Si, K, Cl, S, and Ca were commonly detected in propellants, and Cu and Zn were commonly detected in bullet jackets. Iron might originate from barrel, and the rest of detected elements in GSR might be contamination from other sources such as shooter's hands, target surfaces, or airborne particles [14, 27]. For example, titanium dioxide

is commonly used in paints, cosmetics, food, tooth paste, and the coating of medicine tablets. Thus, Ti is a potential contamination source for GSR recovered from a number of suspected surfaces. Particles containing only two or one of the three unique elements were also detected in a considerable amount. These particles are considered consistent with GSR but not-unique except the Sb-Ba particle. The Sb-Ba particle was classified as characteristic GSR particle by Wolten et al [28]. The detected GSR particles varied not only the elemental composition but the relative amounts of elements detected. The relative amounts of characteristic elements Pb, Sb, and Ba in different "GSR unique" particles from the same test-firing were different. Thus, it is impossible to discriminate different cartridges or identify the cartridge fired using quantitative data of GSR analysis.

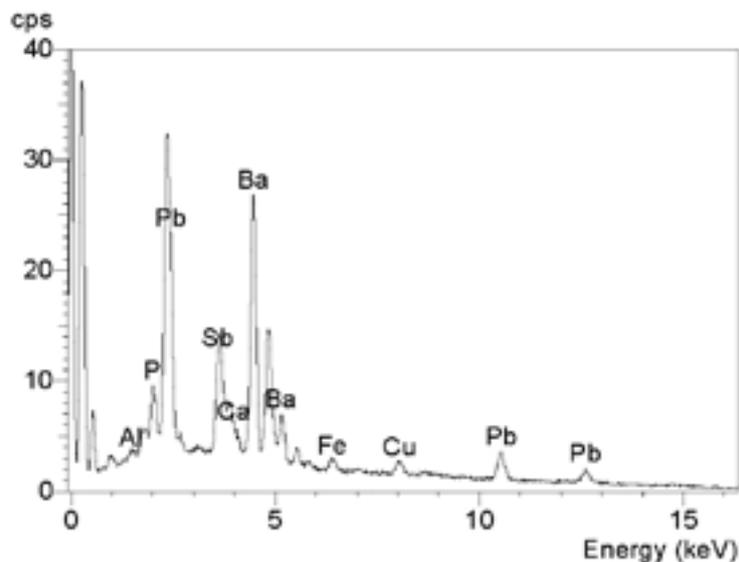


Fig. 10 EDS spectrum of a GSR particle containing Pb, Sb Ba, and some non-GSR-specific elements.

The morphology of GSR particles detected in gun hand and target samples were mainly spheroidal in shape and/or with condensate appearance exhibiting molten features. Most of these particles had a diameter smaller than 10 μm . A typical GSR sphere is shown in Fig.11. GSR particles collected from spent cartridge

cases were usually irregular in shape and present as flakes or aggregated mass with a dimension sometimes bigger than 100 μm . A typical GSR flake is shown in Fig.12. Spherical GSR particles attached to the flakes or randomly distributed around the flakes were frequently observed.

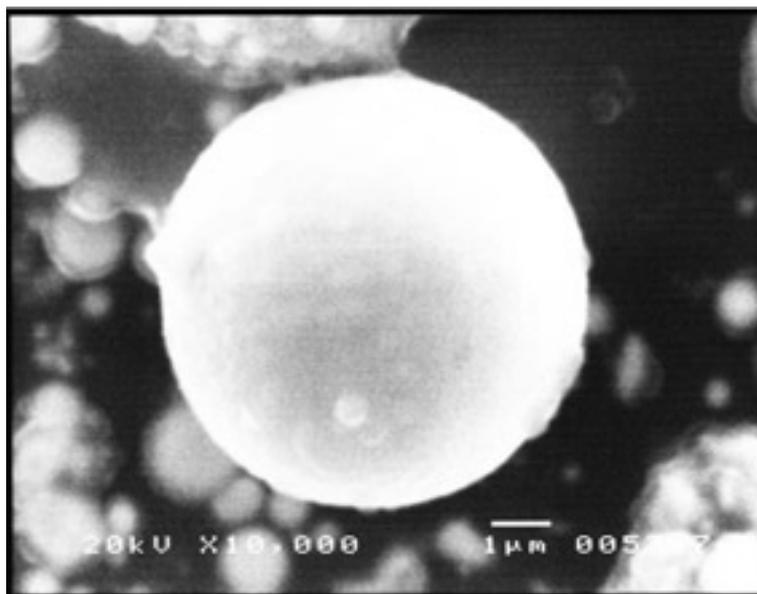


Fig. 11 A spherical GSR particle containing Al, Pb, Sb, and Ba.

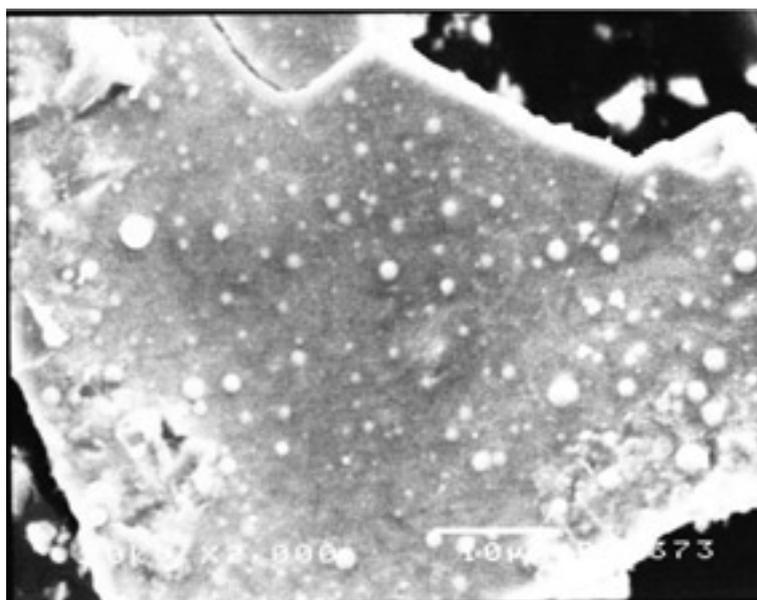


Fig. 12 A flake-shaped GSR from a spent case with numerous fine spheres attached to it.

Unlike the full metal jacketed bullet of common cartridge where the lead core of the bullet is exposed at the base, the lead bullet core of lead-free cartridge is totally enclosed by brass jackets [16]. Both the lead-free primer mixture and the totally enclosed bullet played important roles in preventing the contribution of lead and other heavy metals to GSR particles. Thus no lead-contained GSR particles were detected in any of the GSR samples collected from test-firing of lead-free cartridges. For GSR samples from GFL(02) 9 mm and GFL 38 SPL cartridges, less unique Sb-Ba particles could still be detected (Fig. 13). These Sb-Ba particles were still regarded as GSR specific particles and could be positively identified as GSR when their spherical morphology was simultaneously taken into account [22]. Although it has been reported that unique GSR particles could be detected after firing lead-free cartridges due to the carry-over of Pb-Sb-Ba deposits in the barrel from previous shootings [25], none of Pb-Sb-Ba or Sb-

Ba GSR particles were detected in GSR samples from cartridges of GFL(03) 9 mm, WIN(03) 9 mm, PMP 9 mm, WIN 38 SPL, and WIN 40 S&W in this work. Namely, elements detected in these GSR samples were not specific to GSR, though they were sometimes spherical, and therefore could not be conclusively identified as GSR. This would lead to the difficulty in the investigation of shooting-involved crimes. Fortunately, non-corrosive primers that yield unique GSR particles are still being used by all confiscated illegal cartridges, while police duty cartridges used by domestic police forces are unexceptionally lead-free cartridges. These results indicate that lately developed lead-free cartridges are not currently used by criminals in Taiwan. The significant elemental differences between the GSRs from police duty cartridges and those from the cartridges used by criminals are especially valuable in identifying the responsible shooter whenever the fired bullet is missing.

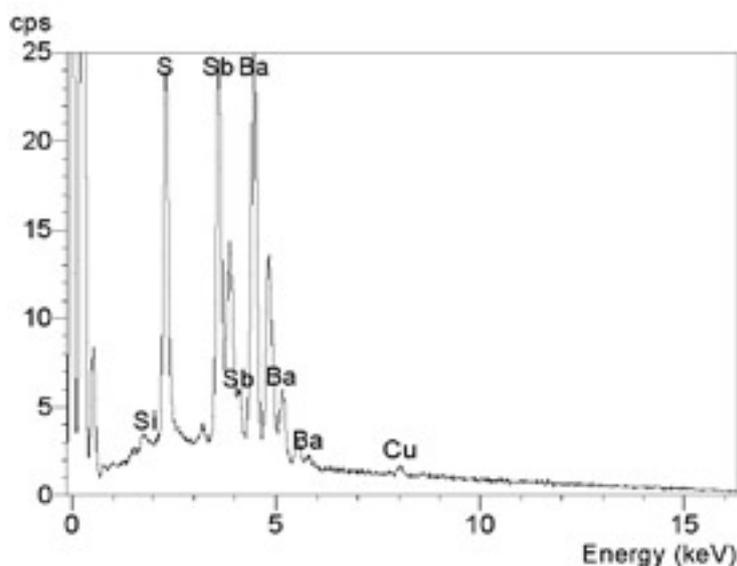


Fig. 13 EDS spectrum of a GSR particle containing Sb and Ba from lead-free cartridge

Although Pb, Sb, and Ba were not detected, some other unusual elements were detected in GSR samples from two lead-free cartridges. Strontium, which is not usually encountered in daily life, was detected in GSR particles generated from PMP 9 mm cartridge (Fig. 14); however it could result from exposure to ignited flares and fireworks, and therefore is still not specific to GSR. Zirconium, which does not have any known connection with GSR at all, was detected in GSR particles from GFL(03) 9 mm (Fig.15). Romolo et al. stated that particles containing elements other than the

permitted accompanying elements were classified as inconsistent with GSR unless the relevant element was present in the GSR from the firearm and/or ammunition used in the crime [7]. In addition to the GSR specific elements Pb, Sb, and Ba, the permitted accompanying elements were defined by Wolten et al. as follows: Si, Ca, Al, Cu, Fe, S, P, Zn, Ni, K, and Cl [28]. Since GSR generated from GFL(03) 9 mm and PMP 9 mm cartridges contained Zr and Sr, respectively, they could be regarded as inconsistent with GSR without the knowledge of the elemental composition of their primer

mixtures. It is obvious that the elemental composition of GSR is primer type dependent. In order to reach a meaningful interpretation of GSR detection results, the comparison of the particles recovered from a suspected surface with those from the cartridge used is even more important than the uniqueness of the particles' elemental composition. The first choice of samples to be compared would be the GSR from the spent cartridge case. Whenever no spent cases are available, it is possible to

detect GSR particles on the bottom of the fired bullet or on the abrasion ring around the bullet hole. If the firearm and/or the cartridge used in the crime are available, primer mixtures and GSR from test-firings should be analyzed for comparative purpose. However, it should be aware that the morphology of primer mixture ingredients and GSR particles from the spent case is not typical of GSR particles observed in case work.

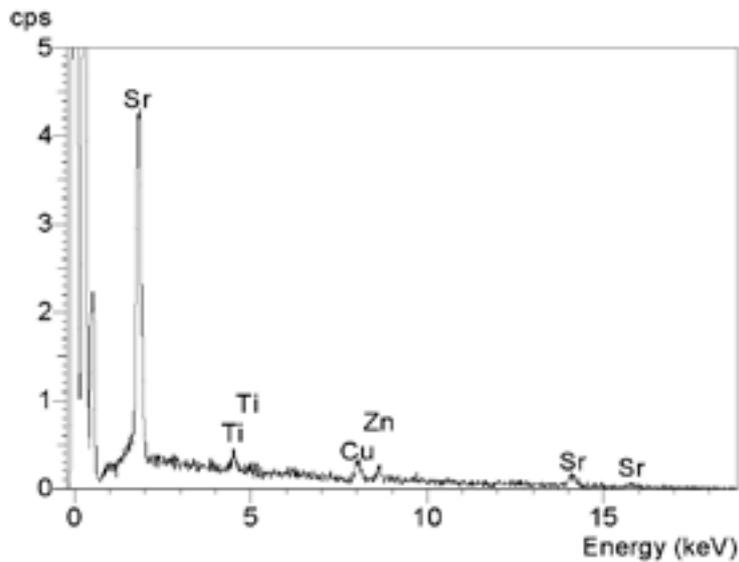


Fig. 14 GSR particles from PMP 9 mm cartridge containing Sr.

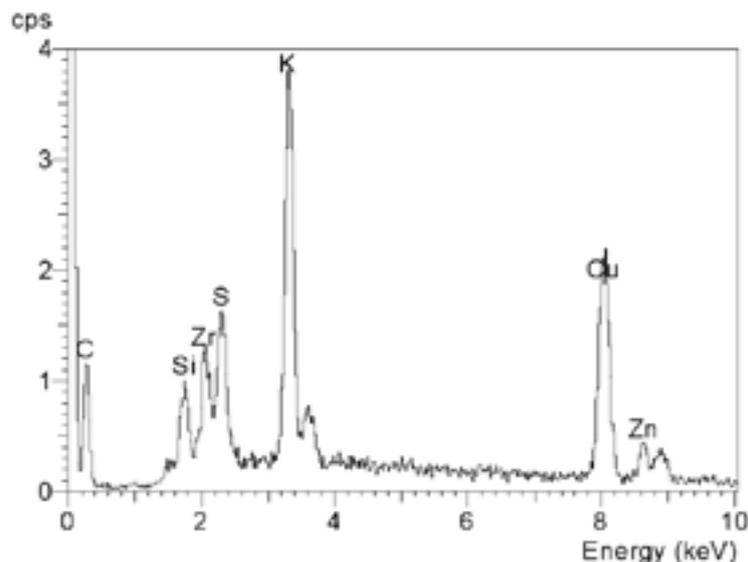


Fig. 15 The unusual element, Zr was detected in GSR from CFL(03) 9 mm cartridge.

Conclusions

Our results revealed that the elemental components of GSR are highly dependent upon the primer type and primer composition of the ammunition discharged. In order to properly interpret the findings of GSR analysis, the comparison of suspected GSR samples with known GSR particles of the ammunition used is even more important than the uniqueness of the particles' elemental composition. The first choice of known samples would be the GSR collected from the spent cartridge case. Comparative GSR samples collected from the bottom of the fired bullet or the target surface around the bullet entrance are also practically useful. Whenever the firearm and the ammunition discharged are available, primer mixture from unfired ammunition and GSR from test firings should also be carefully analyzed. It should be reemphasized that the spherical or spheroidal morphology of GSR particles is as important as their characteristic elemental components for their identification.

It is obvious that the environment-friendly lead-free cartridges, although being unexceptionally used by domestic police force, have not yet been used by criminals in Taiwan. The significant differences of elemental components between GSR from police duty cartridges and cartridges fired by criminals are especially valuable in identifying the responsible shooter while the fired bullet is not recovered. Because the use of lead-free cartridges has become a trend all over the world, these cartridges might soon enjoy general popularity among domestic criminals. The authors suggest that the forensic scientists responsible for routine GSR detection and/or firearms examination should conduct a thorough survey of elemental ingredients of primer mixtures of all confiscated cartridges to prevent false negative conclusions resulted from the use of lead-free cartridges and to facilitate the proper interpretation of GSR analysis findings.

Acknowledgements

The authors are indebted to the National Science Council, Taiwan (ROC) for financial support. The numbers of grants are NSC 93-2745-P-015-005 and NSC 95-2414-H-015-005.

References

1. Sellier K. Shot range determination. In: *Forensic Science Progress*. Berlin: Springer-Verlag, 1991; 6.
2. Deinet W, Lezczynski Ch. Examinations to determine close-range firing distances using a process control computer. *Forensic Sci International* 1986; 31: 41.
3. Bhattacharyya CN. Dispersion of firing discharge residues using a modified Maxwellian model. *Forensic Sci International* 1990; 47: 31.
4. Lichtenberg W. Methods for the determination of shooting distance. *Forensic Sci Rev* 1990; 2: 37.
5. De Forest PR, Martir K, Pizzola PA. Gunshot residue particle velocity and deceleration. *J Forensic Sci* 2004; 49:6.
6. Meng H-H, Caddy B. Gunshot residue detection: A review. *J Forensic Sci* 1997; 42: 553.
7. Romolo FS, Margot P. Identification of gunshot residue: a critical review. *Forensic Sci International* 2001; 119: 195.
8. Meng H-H. The application of scanning electron microscopy/ energy dispersive X-ray analysis to the confirmation of bullet holes. *The 8th Asian Conference on Analytical Sciences, Abstracts*, 2005: 152.
9. DeDonato A, Gutz IGR. Fast mapping of gunshot residues by batch injection analysis with anodic stripping voltammetry of lead at the hanging mercury drop electrode. *Electroanalysis* 2005; 17(2): 105.
10. Nesbitt RS, Wessel JE, Jones RF. Detection of gunshot residue by use of the scanning electron microscope. *J Forensic Sci* 1976; 21: 595.
11. Andrasko J, Maehly AC. Detection of gunshot residue on hands by scanning electron microscopy. *J Forensic Sci* 1977; 22: 279.
12. Lebidzik J, Johnson DL. Handguns and ammunitions indicators extracted from the GSR analysis. *J Forensic Sci* 2002; 47: 483.
13. Zeichner A, Eldar B. A novel method for extraction and analysis of gunpowder residues on double-side adhesive coated stubs. *J Forensic Sci* 2004; 49: 1194.
14. Fojtasek L, Kmjec T. Time periods of GSR particles deposition after discharge-final results. *Forensic Sci International* 2005; 153: 132.

15. Meng H-H, Lee H-C, Chen Y-L. The analysis of primer mixtures and gunshot residues using scanning electron microscopy / energy dispersive x-ray analysis. Proceedings of IEEE Annual International Carnahan Conference on Security Technology, 358, Taipei, Taiwan, 14-16 October 2003.
16. Meng HH, Chen YL. Energy dispersive X-ray analysis of bullets commonly encountered in Taiwan. *Forensic Sci J* 2006; 5: 21. [Full text freely available at: <http://fsjournal.cpu.edu.tw>]
17. Basu S. Formation of Gunshot Residues. *J Forensic Sci* 1982; 27: 72.
18. Zeichner A, Ehrlich S, Shoshani E, Halicz L. Application of lead isotope analysis in shooting incident investigations. *Forensic Sci International* 2006; 158: 52.
19. Harrison H C, Gilroy R. Firearms Discharge Residues. *J Forensic Sci* 1959; 4:184.
20. Wrobel HA, Millar JJ, Kijek M. Identification of ammunition from gunshot residues and other cartridge related materials-A preliminary model using .22caliber rimfire ammunition. *J Forensic Sci* 1998; 43: 324.
21. Powders and primers. In: Lapua reloading manual. Finland: Cartridge Factory Lapua Ltd. 1993; 34,.
22. Wallace JS, McQuillan J. Discharge residues from cartridge-operated industrial tools. *J Forensic Sci Soc* 1984; 24: 495.
23. Liang LY. The chemistry and technology of initiator. China: Beijing Institute of Technology Press, 2004; 226,.
24. Warlow TA. Internal ballistics. In: Firearms, the Law and Forensic Ballistics. London: Taylor & Francis Ltd., 1996; 71.
25. Harris A. Analysis of primer residue from CCI Blazer lead-free ammunition by scanning electron microscopy/energy dispersive X-ray. *J Forensic Sci* 1995; 40:27.
26. Meng H-H, Cheng KC. Unusual characteristics of S&B 9mm Luger cartridge: Ammunition wrongly described by Jane's Infantry Weapons. *J Central Police University* 2000; 36: 401.(In Chinese)
27. Meng H-H, Wu SP. The application of elemental analysis to the identification of propellant powders. *Forensic Sci* 2000; 49: 27. (In Chinese)
28. Wolten GM, Nesbitt RS, Calloway AR, Loper GL, Jones PF. Particle analysis for the detection of gunshot residue. I. Scanning electron microscopy/energy dispersive X-ray characterization of hand deposits from firing. *J Forensic Sci* 1979; 24:409.