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Particle analysis of lighter flint residues using scanning electron microscopy/energy dispersive X-ray spectrometry

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Abstract

The sparking flints used in lighters were reported to generate particles that look like gunshot residue particles. They are spheres and consist of iron and some rare earth metals. Eleven lighters purchased from local stores were used to produce flint residues in this work. The residue samples and flint rods and metal wheels removed from lighters were analyzed using scanning electron microscopy/energy dispersive X-ray spectrometry.

The results reveal that most of the lighter flint residue particles containing rare earth metals are spheroidal. The elemental composition detected in flint residues can be classified into three classes: Al-Fe-Ce-La, Fe-Ce-La, and Fe-Ce. Six lighters produced flint residues containing Fe-Ce-La; four lighters gave residues of Al-Fe-Ce-La; one lighter produced flint residues of Fe-Ce. The results also indicate that the elemental composition of lighter flint residue is highly correlative with the composition and construction of the flint rod.

The lighters' flint rods are made of ferrocerium containing iron and rare earth metals which are scarcely encountered in daily life. The detection of spheroidal particles containing iron and rare earth metals provides a way to identify lighter flint residues. These characteristic residues can be used as trace evidence in crime cases where the linkage between a lighter user and another persons or places is to be established. Furthermore, since the elemental profile of lighter flint residues is totally different from that of GSR, the lighter flint residues would not affect the identification of gunshot residues at all.

Keywords: forensic sciences, trace evidence, particle analysis, lighter flint residues, gunshot residues, scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS)

Introduction

Inorganic gunshot residues (GSR) consist of discrete, micrometer-sized particles, predominantly spheroidal, and often of characteristic appearance. These GSR particles 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 while discharging a firearm [1,2]. The unique elemental profile and characteristic spherical shape of GSR are usually identified using scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) which allows the identification of a single GSR particle in non-destructive way and gives a high selectivity unparalleled by any bulk analysis methods. The energy dispersive X-ray analyzer is able to identify all elements heavier than sodium contained in GSR particles. Elemental composition of lead, antimony, and barium has been observed only in gunshot residues and are therefore considered characteristic of GSR [3]. The spheroidal morphology of the particles allows them to be discriminated from the general debris lifted from the hand and other surfaces under the secondary electron imaging mode, and the higher atomic numbers of their characteristic elements allow them to be found as brighter particles among the darker background under the backscattered electron imaging mode.

An article published in New Scientist magazine in 2005 argued about the probative value of forensic examination of gunshot residues. The article raised a number of critical issues including the uniqueness of

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GSR particles, criteria for the identification of GSR, contamination of GSR via secondary transfer and environmental and occupational particles [4]. A number of environmental and occupational particles that might interfere the identification of GSR have been examined [5, 6, 7, 8, 9, 10, 11]. These interfering particles might originate from stud guns, cap guns, pyrotechnics, brake linings, lead smelting, lead-acid battery, and lighter flints. In late 1970s, research results indicated that none of these environmental and occupational samples was falsely identified as gunshot residue by the experienced analysts; however, less experienced personnel may sometimes have encountered difficulties [6]. However, later literatures revealed that elemental profiles of brake linings and pyrotechnics are similar to that of GSR. A feasible technique employed to distinguish these particles from GSR particles is X-ray mapping [7, 8, 9]. Elemental profile is the most definitive characteristic of a GSR particle, thus micrometer-sized spheroidal particles of various origins other than GSR are usually easily excluded as being composed of elements other than lead, barium, and antimony and do not constitute a problem [3]. Lighter flint residue is one kind of these non-Pb-Ba-Sb micrometer-sized spheroidal particles which has been regarded as being with a clearly identifiable separate origin [5]. The sparking flints used in cigarette lighters were reported to generate particles that look like GSR particles under the SEM observation during the ignitions of the lighters. They were described as being spheres, sometimes porous like a sponge, and consist of iron and some rare earth elements [6]. The same article also revealed that lighter flint residues were occasionally found on the hand of a nonsmoker. According to Locard's Exchange Principle whenever a person comes into contact with an object or another person a cross-transfer of physical evidence occurs. By searching, recognizing, collecting, and examining the transferred evidence criminals could be linked with crime scenes and victims [12]. This brings out a possibility that lighter flint residue can be used as a trace evidence to confirm possible contacts between a lighter user and another persons or objects. This work focused on the SEM/EDS analysis of lighter flint residues collected from the surface of used lighter and hand of the user. Hopefully, the results of this work would provide a practical way to identify the lighter flint residue evidence on crime cases where a lighter user is involved.

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 (EDX), Oxford, UK. X-ray signals were collected from 0 to 20 KeV, 20 eV per channel. Peaks were either manually or automatically identified.
3. Ten disposable lighters and one military-typed lighter were used in this work. One disposable lighter and the military-typed lighter are shown as Figs. 1 and 2. Details of lighters employed for test ignitions and samples analyzed are shown in Table 1.

Table 1 Details of lighter and samples analyzed.

Sample name	Brand [a]	Type of lighter	Samples analyzed
D1	弼臣	Disposable	Flint residues
D2	弼臣	Disposable	Flint residues
D3	千輝	Disposable	Flint residues
D4	千輝	Disposable	Flint residues & flint rod
D5	萬達	Disposable	Flint residues
D6	鴻興	Disposable	Flint residues
D7	永輝	Disposable	Flint residues& flint rod
D8	勇士	Disposable	Flint residues
D9	千輝	Disposable	Flint residues
D10	旭輝i	Disposable	Flint residues
M1	Zippo	Military	Flint residues

Fig.1 A typical disposable lighter used in this work.

Fig.2 The military-typed lighter used in this work.

Methods

1. Analysis of flint residues: The metal wheel of each lighter was rolled to strike against the flint rod to ignite the brand new lighter for five times. Lighter flint residues were then collected from the thumb and the web of the user's igniting hand and the surface around the flame port of the lighter using SEM sample stubs attached with double-sided carbon tape. Lighter flint residue samples were then coated with carbon prior to SEM/EDS analysis. Blank samples for each lighter tested were also collected from the user's previously cleaned hand before test ignitions were performed and these blank samples were subsequently subjected to carbon coating and SEM/EDS analysis.
2. Analysis of flint rods: After the analyses of flint residue samples were completed, flint rod and metal wheel from D4 and D7 disposable lighters were removed from the lighters. Each of these parts was mounted on one SEM sample stub using double-sided carbon tape. Mounted samples were coated with carbon and subjected to SEM/EDS analysis.

Results and discussion

Analysis of flint residues

There were no spheroidal particles observed in all blank samples. Most of the particles in a sample of lighter flint residues that contained rare earth metals had spheroidal morphology. The samples collected around the flame ports of ignited lighters were most abundant of spheroidal particles with a wide range of sizes (Fig. 3). For samples collected from user's hand, more spheroidal particles were detected on thumb samples than web samples. This indicates that direct contact between thumb and metal wheel transfers more flint residues toward user's hand than flint residues carried by sparking toward the hand. For all three samples originated from the test ignitions of D4 lighter, there were only several spheroidal particles containing rare earth metals detected in each sample. This lighter was thus disassembled and the flint rod and the metal wheel were removed for further SEM/EDS analysis to find out the reason of relatively small amount of spheroidal residue particles produced during test ignitions. The results are described later in this work.

Spheroidal particles observed may be perfect spheres, or their morphology may be slightly deviated from perfect sphere, but "three-dimensional roundedness" is a required feature of this classification. The surfaces of the spheroids may be smooth, rough, or attached with smaller spheres. Occasionally, they are hollow or perforated spheres. Examples of different shaped spheroidal flint residue particles are shown as Figs. 4-8. The diameters of the spheroidal particles detected were usually less than 30 μm. Because of the limitation of the resolution of SEM used, particles less than 0.5 μm in diameter were not analyzed in this work. The

morphology of spheroidal lighter flint residue particles is nearly the same as that of gunshot residue particles. Thus flint residues cannot be differentiated from GSR solely through morphological comparison. Two typical spheroidal GSR particles are shown in Figs. 9 and 10 for comparative purpose.

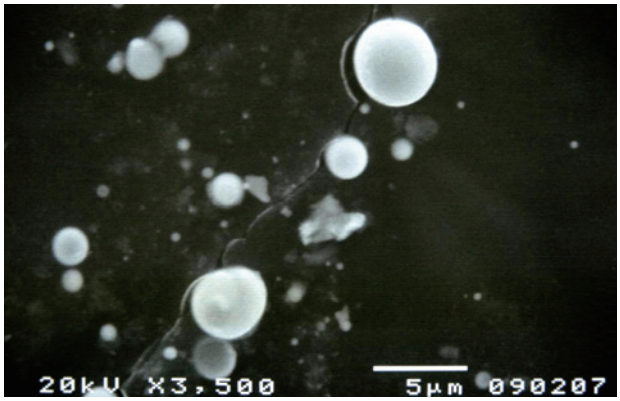

Fig.3 The sample collected around flame port of an ignited lighter is abundant of different sized spheroidal particles.

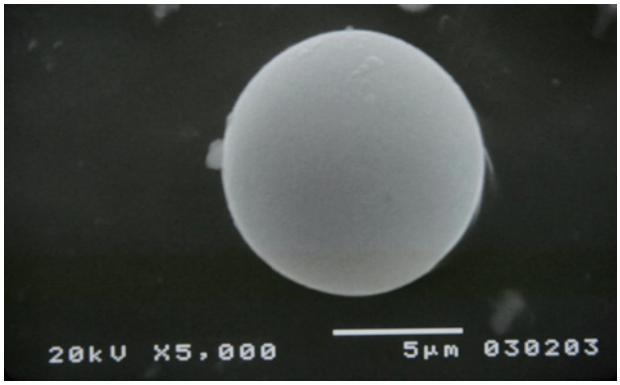

Fig.4 A perfect lighter flint residue sphere.

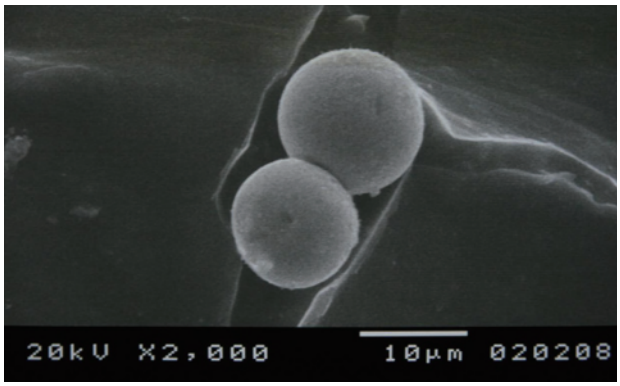

Fig.5 Two spherical lighter flint residue particles connected to each other.

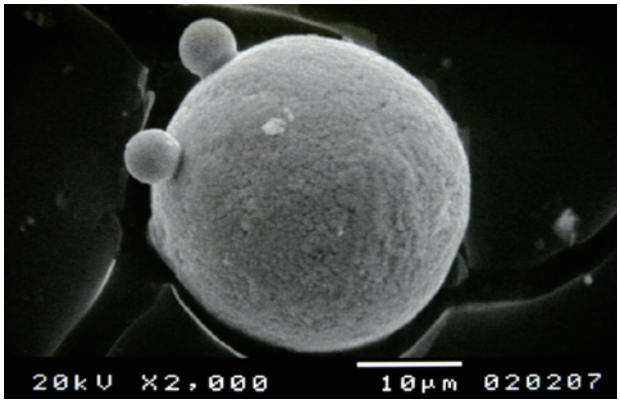

Fig.6 A spherical lighter flint residue attached with smaller spheres.

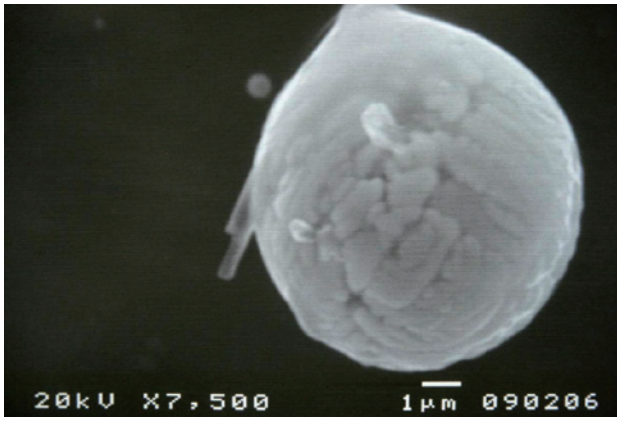

Fig.7 A rough surfaced spheroidal lighter flint residue particle.

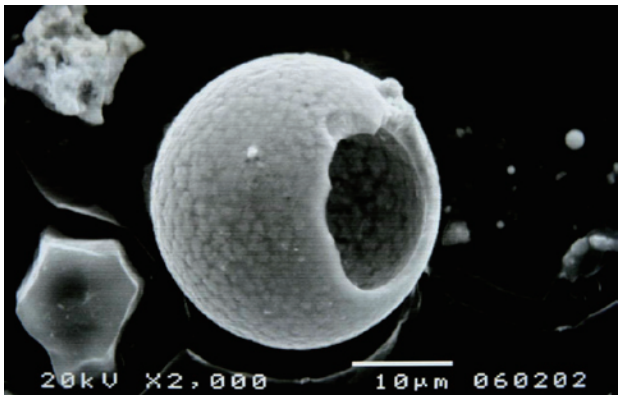

Fig.8 A broken hollow lighter flint residue sphere.

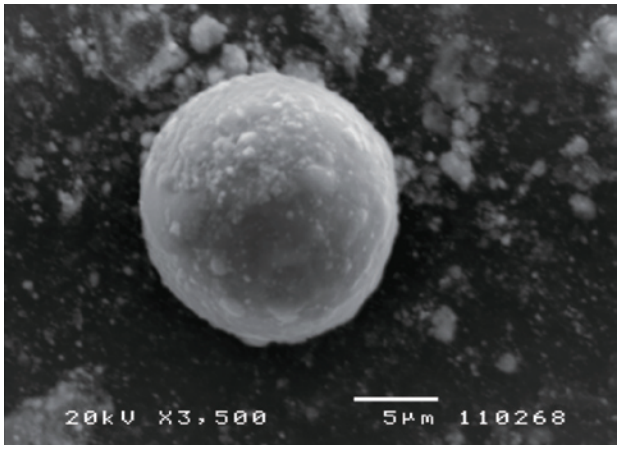

Fig.9 A rough surfaced spherical GSR particle.

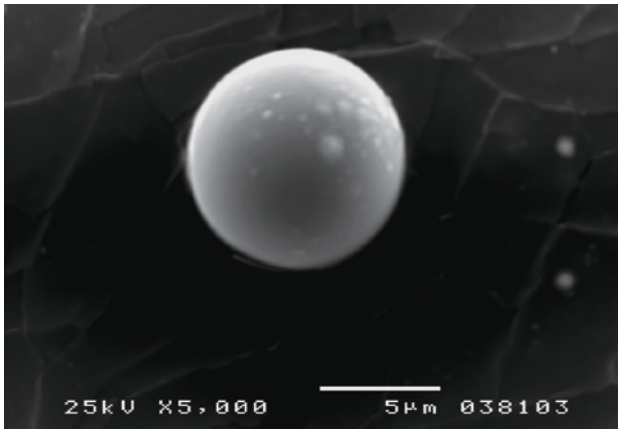

Fig.10 A smooth surfaced spherical GSR particle.

The details of elements detected for the lighter flint residue samples from test ignitions of various lighters are shown in Table 2. Major elements detected in lighter flint residue samples collected from flame port, user's thumb, and user's web after test ignitions of each lighter are in perfect accordance with each other. The elemental composition detected in flint residues from the eleven lighters studied can be classified into three classes: aluminum-iron-cerium-lanthanum (Al-Fe-Ce-La), Fe-Ce-La, and Fe-Ce. Six out of eleven lighters produced flint residues that contained Fe-Ce-La. Four out of eleven lighters gave residues containing Al-Fe-Ce-La. Aluminum is not a required component for either flint rod or metal wheel. The D7 lighter was thus disassembled and the flint rod and the metal wheel were removed for further SEM/EDS analysis to find out the source of Al in the residues. The D8 lighter is the only one that produced the flint residues having the simplest elemental profile of Fe-Ce.

Flint rod of a lighter is made of ferrocerium that is a man-made metallic material and is able to give off a quantity of hot sparks when struck against the metal wheel. When small shavings of the flint rod are removed quickly enough, the heat generated by friction is enough to ignite those shavings. The sparks generated are actually micro droplets of liquidized burning metal that condensed into solid spheres after cooling down. These spherical particles would deposit on the surface of the lighter and the user's hand, or any objects close to the igniting lighter. Modern ferrocerium product is usually composed mostly of iron, combined with an alloy of rare earth metals such as cerium, lanthanum, and neodymium. The origin of easy sparking of ferrocerium flint is cerium's low temperature pyrophoricity, its ignition temperature occurring between 150 and 180℃ [13]. There are two more types of ferrocerium flint manufactured, the first contains just iron and cerium, and the second also includes lanthanum to produce brighter sparks. Since the flint residues are formed in a very short period of time, the reduction-oxidation reaction of the burning of the flint rod shavings has never reached its equilibrium; the elemental composition of residue particles may be different from each other even they are produced from the same lighter. In spite of this, the qualitative elemental profiles of residue particles detected can still be classified into six categories as followings: (1)Fe-Ce-La; (2)Ce-La; (3)Al-Fe-Ce-La; (4)Al-Ce-La; (5)Al-Fe-Ce; (6)Fe-Ce. Typical energy dispersive X-ray spectra of every elemental profile are shown in Figs. 11-16. Particles have elemental profiles of Fe-Ce-La and Ce-La occurred in all flint residue samples except that from lighter D8. Since elements Ce and La are scarcely encountered in daily life, this elemental profile can be regarded as the most characteristic elemental composition of lighter flint residue. Particles contained Al occurred only in samples collected from test ignitions of lighters D6, D7, D10, and M1. For samples originated from lighter D8, only Fe-Ce particles were detected.

Table 2 Elements detected in flint residues collected from various lighters.

Sample name	Elements detected
D1	Fe, Ce, La
D2	Fe, Ce, La
D3	Fe, Ce, La
D4	Fe, Ce, La
D5	Fe, Ce, La
D6	Al, Fe, Ce, La
D7	Al, Fe, Ce, La
D8	Fe, Ce
D9	Fe, Ce, La
D10	Al, Fe, Ce, La
M1	Al, Fe, Ce, La

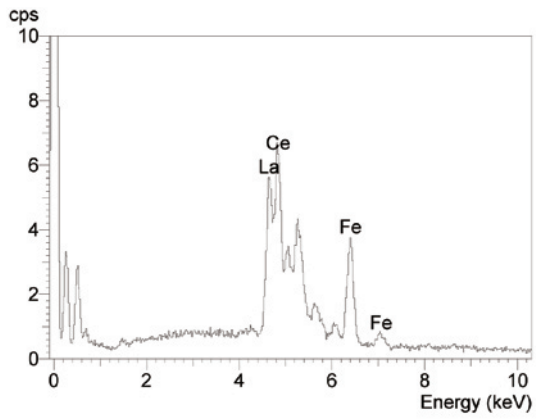

Fig.11 An EDS spectrum of lighter flint residues containing Fe, Ce, and La.

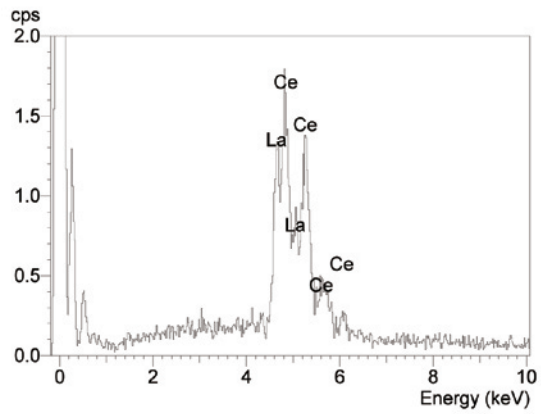

Fig.12 An EDS spectrum of lighter flint residues containing Ce and La.

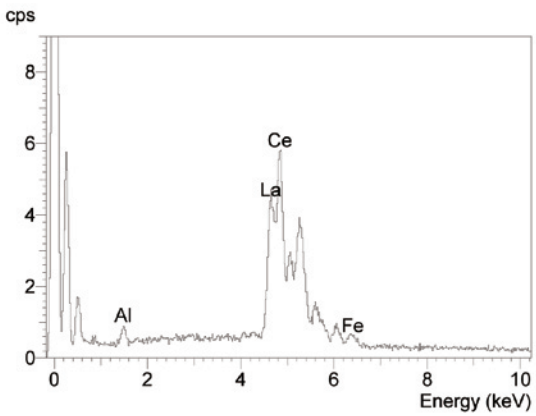

Fig.13 An EDS spectrum of lighter flint residues containing Al, Fe, Ce, and La.

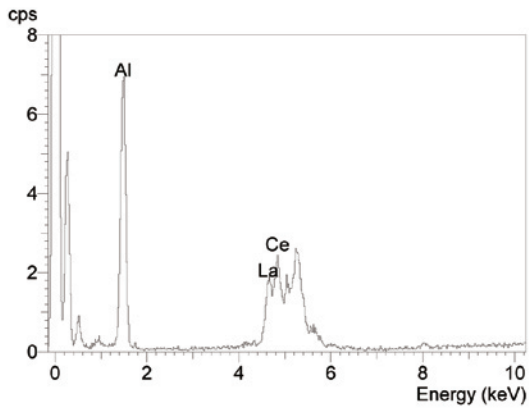

Fig.14 An EDS spectrum of lighter flint residues containing Al, Ce, and La.

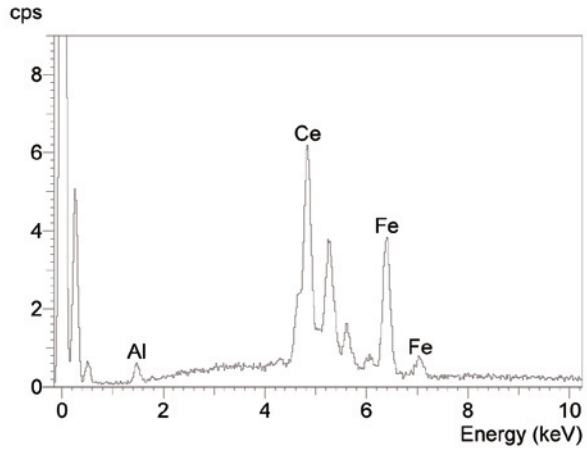

Fig.15 An EDS spectrum of lighter flint residues containing Al, Ce, and Fe.

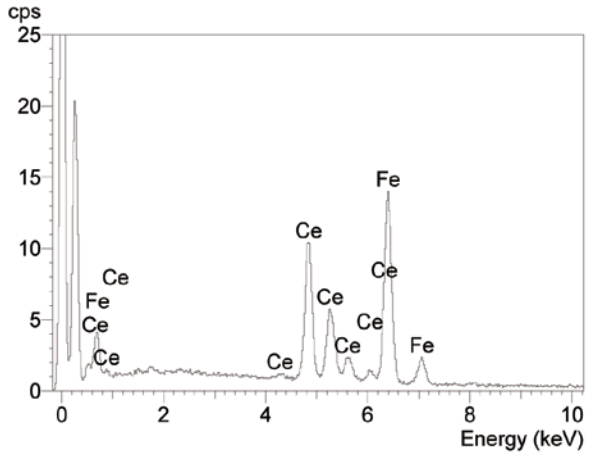

Fig.16 An EDS spectrum of lighter flint residues containing Fe and Ce.

Analysis of flint rods and metal wheels

In addition to carbon element, the major elements detected on the cross section of flint sample D7 are Fe, Ce, and La. A typical energy dispersive X-ray spectrum of flint rod is shown in Fig. 17 where carbon peak is not labeled. The only element detected on the rim of the flint rod is aluminum. This showed that the flint rod is wrapped with a layer of aluminum and this aluminum layer is the source of the Al detected in flint residues originated from lighters D6, D7, D10, and M1. For lighter flint sample D4, with the exception of the major peak of carbon the intensity of detected peaks is so low that these peaks can barely be identified as Fe, Ce, and La. It is thus assumed that the concentration of ferrocerium metal in D4 flint rod, which is basically a carbon rod, is relatively low and close to the detection limit of EDS technique. This result explained the reason why only a small amount of characteristic flint residue particles were detected in samples collected from the test ignitions of lighter D4. The results of flint rod analysis also indicate that the elemental composition of lighter flint residue is highly correlative with the composition and construction of the flint rod. Both D4 and D7 metal wheel samples were found to contain iron and zinc (Fig. 18).

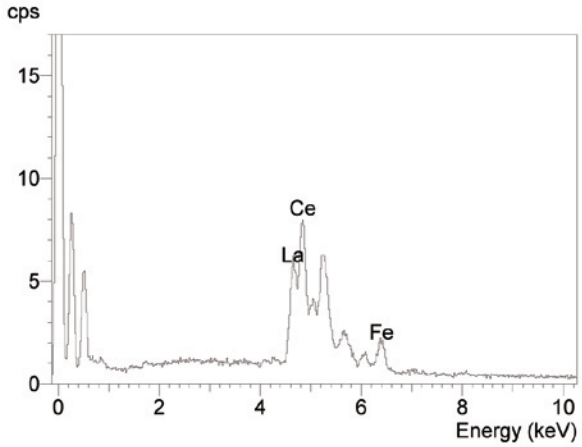

Fig.17 An EDS spectrum of elements detected on lighter flint sample D7.

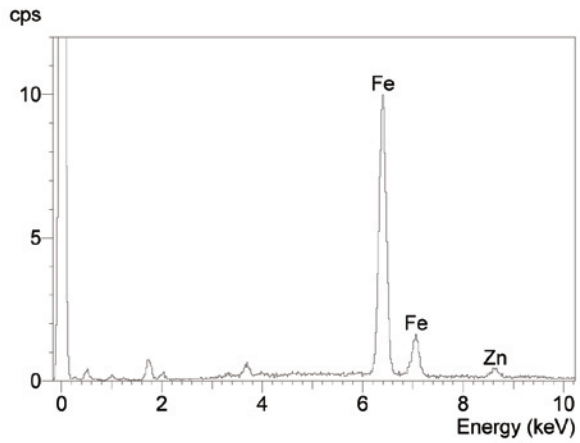

Fig.18 Metal wheel contains iron and zinc.

Conclusions

Our results reveal that the elemental components of lighter flint residues are highly dependent upon the composition and construction of flint rods. The flint rods of modern lighters, regardless disposable ones or military-typed ones, are composed of ferrocerium containing at least one rare earth metal of cerium. In most of the cases, flint rods contain rare earth metals of cerium and lanthanum. Since Ce and La are scarcely encountered in daily life and spheroidal micro particles result only from high temperature events, the detection of spheroidal particles containing iron and rare earth metals using SEM/EDS provides a way to confirm the presence of lighter flint residues. These characteristic residues can be used as trace evidence in any crime cases where the linkage between a lighter user and another persons or places is to be established.

It is obvious that, although the morphology of lighter flint residue particles is almost the same as that of GSR particles, the elemental profile of lighter flint residues is totally different from that of GSR. It can be concluded that the lighter flint residues are not the sources of interferences toward the identification of gunshot residues.

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