

TECHNICAL NOTE

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A Versatile Technique for the Investigation of Gunshot Residue Patterns on Fabrics and Other Surfaces: m-XRF

ABSTRACT: With heavy-metal-free ammunitions becoming more and more popular, it is necessary to find methods to visualize patterns of those elements in gunshot residues (GSRs) that are not accessible by chemographic coloring tests. The recently introduced millimeter-X-ray fluorescence analysis (m-XRF) spectrometer *Spectro Midex M* offers an easy way to record mappings of GSRs containing such elements in order to determine shooting distances as well as the general composition of these particles. A motorized stage enables samples of a maximum size of 20 × 20 cm to be investigated, like fabric, clothes, adhesive tapes (Filmolux[®] films), and polyvinylalcohol gloves of shooter's hands. Human tissues can be measured using a Peltier-cooled specimen holder that is mounted onto the stage. As the spot size of the exiting X-rays lies in the millimeter range, which is adequate for the assessment of the residue patterns for shooting distance determination, a significant reduction in measurement time is achieved compared with μ -XRF methods. Test shots with heavy-metal-free ammunitions were performed on different target materials, like pork skin and fabric, and the elemental distributions of Ti, K, and Ga were determined. In order to show the capability of the spectrometer for conventional lead ammunitions as well, a shot series of 5–100 cm shooting distance and an adhesive tape of a shooter's hand were investigated analogously. A comparison of several methods applied in GSR investigation shows the advantages of the m-XRF method.

KEYWORDS: forensic science, gunshot residues (GSRs), X-ray fluorescence analysis (XRF), shooting distance, Sinoxid ammunition, lead-free primers

There follows a description of the use of the X-ray fluorescence spectrometer *Spectro Midex M* (Spectro Analytical Instruments, Kleve, Germany) (1) as well as its application for the investigation of gunshot residues (GSRs). This X-ray fluorescence analysis (XRF) spectrometer provides the possibility of recording elemental mappings of samples up to 20 × 20 cm in size. Such distribution patterns are used in GSR investigation, e.g., for shooting distance estimation.

In order to demonstrate the capabilities of the millimeter (m)-XRF, a series of test shots was prepared using various types of fabrics with ammunitions of conventional primers (containing Pb, Ba, and Sb) as well as modern nontoxic primers not detectable by the common chemographic methods. Adhesive films (e.g., Filmolux[®], Neschen AG, Buckeburg, Germany) were used to demonstrate an alternative means to collect GSR for further analysis.

An additional field of application is the investigation of human tissue for GSR. Samples can be cooled by a Peltier-cooled cryostage in order to minimize odor effects due to the potential decomposition of the tissue during measurement.

Method

Instrument

For present investigations, the energy-dispersive X-ray fluorescence spectrometer, *Spectro Midex M*, was applied (1). As an X-

ray source, a 30 W Mo-tube (maximum 50 kV, maximum 0.6 mA) is used. A set of collimators with quadratic cross-sections of 0.1, 0.3, 0.5, and 1 mm (with and without Nb-filter) results in spot sizes on the sample of 0.2, 0.6, 1, and 2 mm, respectively. The Nb-filter reduces the background signal in order to improve the detectability of the Pb-L series. The detector is a Peltier-cooled Si-drift detector (SDD) with an energy resolution of 150 eV (Mn K_α). The measuring time is adjustable, depending on the type of sample and the desired resolution. Especially if a digital background subtraction is necessary after the measurement, a recording time of at least 3 sec per point is needed. The sample area can be chosen within a frame of 20 × 20 cm. Usually, the entire sample is not scanned but only the interesting region around the bullet wipe ring. To adjust the proper working distance of the sample, two crossed laser pointers and a video camera are used. The camera also shows the area in progress for the investigated sample. A second video camera provides an overview image of the entire sample in order to select the region to be analyzed. All measurements shown below were carried out in air. The system is also equipped with a Helium purge system, in case light elements are to be detected.

Modes

Three different modes are available: point scan, line scan, and mapping. The point scan mode is used to identify the elemental composition of GSR, choosing long measuring times for the best resolution. Line scans are applicable to give a rough idea of the shooting distance, scanning along a line through the wipe ring,

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and helping to identify the entrance hole of a bullet. Although point scan and line scan modes are useful to carry out a quick survey for GSR-related elements, the more time-consuming mapping mode provides detailed information of the GSR distribution on the sample. After recording an element mapping, a statement on the distribution of all elements of interest can be made and, subsequently, a more precise estimation of the shooting distance.

Sample Holder—Clothing

To keep thin materials like fabrics and foils at an appropriate position during measurement, a special specimen holder (Fig. 1a) was designed. The samples are stretched over the frame and kept in place by clamps, so no mechanical support at the point of measurement is necessary, resulting in a reduction of the background signal. Also, the investigation of very small samples is possible due to a retractable polyethylene sheet, on which, for example, pieces of fabric or polyvinylalcohol (PVAL) gloves (2) can be placed. To hold these samples fixed in a particular position, a common plastic wrap can be applied, which has the advantage of being easy to use and to dispose of in the case of contamination.

If GSRs are expected on clothes, it is no longer necessary to cut out the regions of interest, as these samples can also be investigated using a specially designed holder for clothes without damaging the sample. The sample chamber of *Midex M* (Fig. 1b) is large enough to enable the investigation of, for example, jackets, trousers, etc.

Sample Holder—Tissue

Human tissue needs a special kind of sample holder, because it requires cooling during measurement. A gel-filled cryo-table is mounted on a Peltier-element (Fig. 1c), cooling the gel down to a temperature of *c.* 4°C. The viscosity of the gel provides a suitable surface for the measurement of human tissue samples as the amount of gel inside the table is variable to compensate for inhomogeneity in sample thickness and to adjust the height of the sample. On top of this table, the tissue is fixed using a plastic wrap. The maximum sample size is limited to 14 × 14 cm but also very small samples can be investigated using additional inserts in the gel matrix.

Results and Discussion

To illustrate the advantages of the m-XRF system for the investigation of GSRs, this method is compared with common chemographic imprinting (3–5), conventional XRF (6), and μ -XRF (7) methods applied in the investigation of GSR. For a clearer overview, the results are listed in Table 1.

The range of detectable elements using m-XRF is similar to μ -XRF and conventional XRF, which are methods for multielement analysis in contrast to chemographic methods. But chemographic imprinting is much faster in application than μ -XRF and conventional XRF. The speed of m-XRF is between that of μ -XRF and conventional XRF, depending on the selected measurement settings. Compared with chemographic or μ -XRF methods, the resolution of the m-XRF is lower but adequate for the application described. Also, the sample preparation is very easy, as most of the samples do not need any preparation compared with chemographic methods in particular. A special feature of the m-XRF is the short time of recording elemental mappings on the sample, which can also be performed by μ -XRF, or chemographic imprints. These methods, however, are time consuming or applicable for only a few chemical elements.

The m-XRF method combines features like resolution, speed, detectable elements, sample preparation, and elemental distribution mapping considering the demands for GSR investigation in a manner that makes it very attractive to forensic labs. To explore the capabilities of the X-ray fluorescence spectrometer *Midex M*, several sample sets using different substrates were prepared: GSRs were investigated on fabrics and other surfaces like foils, as well as on pork skin.

Especially for the investigation of conventional lead primers, the *Midex M* is also equipped with a Nb filter (2 mm spot size only) that reduces the intensity of the continuous radiation in a window from *c.* 10 to 15 keV. Thus, the detection of the Pb-L series is enhanced.

Investigation of GSRs Patterns on Fabrics and Foils

Ammunition with Pb-containing primers was used to compare the elemental distribution in the *Midex M* mapping with the conventional rhodizonate test. Different samples were prepared (target: cotton, ammunition: Geco 9 mm × 19 FMJ with Sinoxid primer, shooting distances: 5, 20, 40, 60, 100 cm). Figure 2 shows the distribution of Pb and Ba (shooting distance: 5 cm) detected with the *Midex M* in mapping mode (measurement time: 2 s/point only intensities, no background subtraction, 50 kV, spot size 2 mm with Nb-filter) compared with the common chemographic imprint (Fig. 2b). Chemographic imprint and XRF mapping show similar distributions of Pb (Fig. 2). Around the bullet hole, the wipe ring is visible in addition to a nearly circular GSR cloud with “halo”-formation, typical for short-range shots. Barium (red-orange color) is only visible near the entrance hole in the chemographic imprint. In contrast to this, the Ba-mapping reveals that Ba is also present in the GSR cloud, decreasing as the distance from the bullet hole increases. Thus, the intense purple color of Pb masks the Ba-distribution in the chemographic imprint.



FIG. 1—Two sample holders and the sample chamber of the millimeter-X-ray fluorescence analysis (m-XRF) Spectro *Midex M*—(a) Clamp frame for the investigation of gunshot residue (GSR) on fabrics and adhesive tapes, (b) Spectro *Midex M*: sample chamber, (c) Peltier-cooled sample holder for the investigation of GSR on tissues.

TABLE 1—Comparison of common chemographic methods, conventional XRF, μ -XRF, and m-XRF for application in GSR investigation.

	Chemographic Methods	μ -XRF	Conventional XRF	m-XRF (<i>Midex M</i>)
Range of detectable elements	Limited to available reagents	Nearly all elements detectable with XRF	Nearly all elements detectable with XRF	Nearly all elements detectable with XRF
Speed	~ 30 min	Days	Min*	~ 4 h
Resolution	~ 10 μ m	μ m-range	30–40 mm [†]	0.2–2 mm
Sample preparation	30 min	No preparation	Punch out pieces	No preparation
Element mappings	Yes	Yes	No*	Yes
Large area investigation	Up to 40 \times 40 cm	Limited by sample chamber	No* [†]	Now: 20 \times 20 cm (limited by sample chamber)

*No pattern available.

[†]Integral measurement.

GSR, gunshot residue; m-XRF, millimeter-X-ray fluorescence analysis.

The usual measurement time is approximately 4 h, which is rather long compared with the chemographic method, but it enables the detection of all elements simultaneously. Additionally, as X-ray fluorescence is a nondestructive method, the samples are still available for further investigations after the measurement. The mappings obtained by m-XRF measurements can be used for the evaluation of the shooting range estimation in the same way as with chemographic imprints. The shooting distance of an unknown sample is estimated by visual comparison of its GSR-pattern with a series of test shots at known shooting distances (6).

Figure 3 shows an example of range-dependent GSR-patterns. In Fig. 3, the mappings of shooting distances from 5 to 100 cm are listed. The 5 cm shot is used to show an X-ray spectrum of a point scan (measuring time: 100 s/point, collimator size: 0.6 mm) near the bullet wipe ring (Fig. 4a). A long analysis time was chosen to achieve good resolution and unambiguous elemental identification. Elements detected were Pb, Ba, and Sb as well as Cu originating from the bullet jacket.

A line scan across the sample gives a first impression of the shooting distance and identifies the damage as a bullet hole (see Fig. 4b). Pb is detected around the damage and also the disparity in Pb-concentration can be seen in this evaluation.

Shooting range estimation with *Midex M*-mappings is not limited only to visual pattern matching. As intensity information of every point in the mapping is available, the data can be processed in various ways to obtain additional information by using common data processing programs like EXCEL or Origin. An example of the calculation of average impulse rates for a specific area on the sample is shown in Fig. 4c. Another application is to calculate the radial distribution of impulse rates of a specific element around the bullet hole (Fig. 4d).

Numeric values obtained by the calculation of average impulse rates can be used similarly for the application of a conventional wavelength-dispersive (WD)-XRF spectrometer in shooting range estimation. The “impulse rate” as a function of the shooting distance is determined and can be used to estimate the unknown shooting distance, keeping in mind that the original particle concentration can change due to sample handling. Although the sensitivity and accuracy of the m-XRF are lower than a WD-XRF, it is not necessary to cut the evidence into pieces to perform the measurement. Instead of this, the specimen can be investigated without any damage and the area of interest is selected in the software application.

Radial distribution can be interpreted as an abstraction or simplification of a GSR-pattern by calculating the average impulse rate at specific distances from the bullet hole. This enables the identification of range-dependent features in the GSR distribution, like the so-called “halo”-formation and facilitates the comparison of incomplete GSR patterns (e.g., entrance hole in the corner of a specimen) with test shots.

Another advantage of X-ray fluorescence methods compared with chemographic methods is the detection of elements like Ti or K that cannot be visualized as a contrast by common coloring reagents (8). As ammunitions with nontoxic primers are becoming more common, this kind of investigation is growing in the field of GSR investigation. Figure 5 shows mappings of shots from lead-free ammunition like RUAG’s “Action 4,” MEN’s “QD-PEP IIs,” and S&B’s “Nontox” at a distance of 5 cm. The ammunition “Action 4” contains Ti in the primer, which is detected mainly near the bullet wipe ring. Ga is added to the “QD-PEP IIs” as a dopant/tracer to the propellant to generate characteristic GSR-particles. Additionally, the “Nontox” ammunition containing only

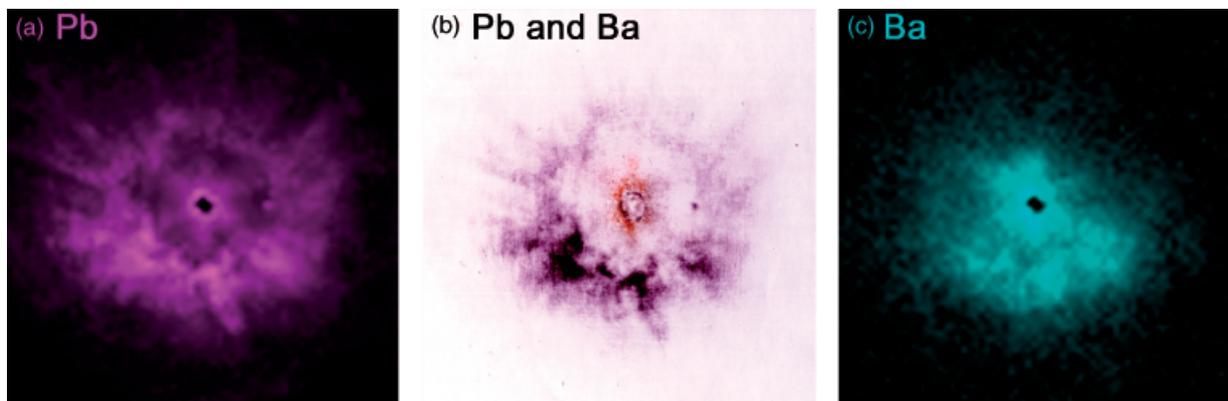


FIG. 2—Comparison of *Midex* mapping and chemographic imprint (mapping/imprint size: ~ 14 \times 14 cm, collimator: 2 mm Nb-filter)—(a) X-ray fluorescence analysis (XRF) mapping of Pb, (b) Rhodizonate imprint using SPM: Pb (purple), Ba (red), and (c) XRF mapping of Ba.

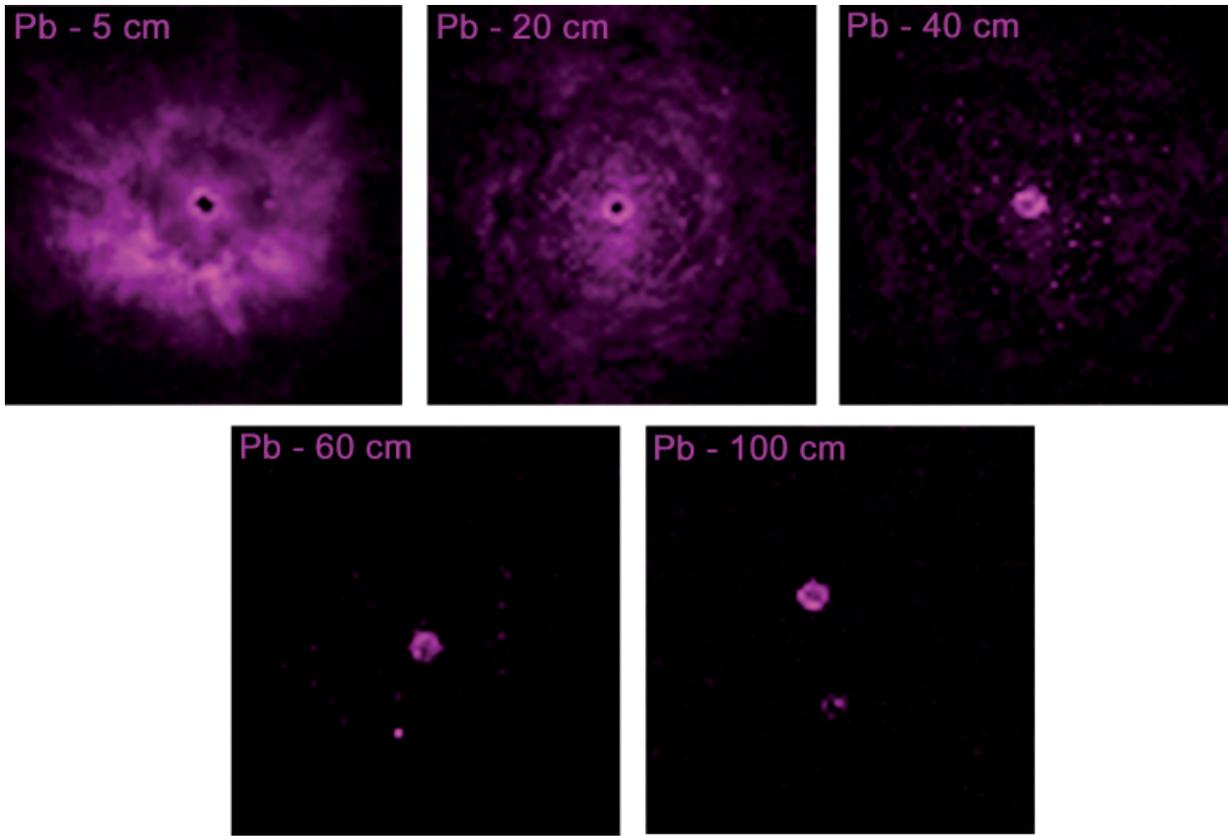


FIG. 3—Series of shots from different distances (5–100 cm), X-ray fluorescence analysis mapping of Pb, mapping size: $\sim 14 \times 14$ cm, collimator: 2 mm Nb-filter.

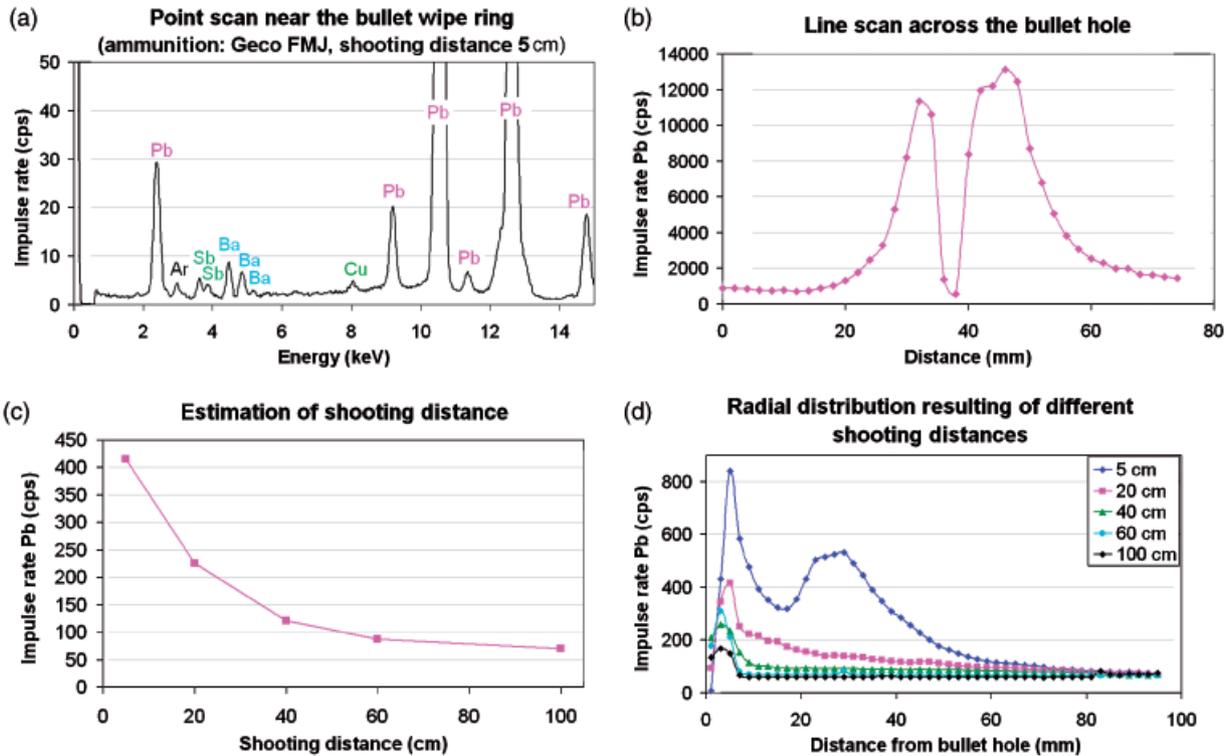


FIG. 4—(a) X-ray spectrum of a point scan (shooting distance: 5 cm, collimator: 0.6 mm), (b) Mapping of a line scan across the bullet hole (shooting distance: 5 cm, collimator: 2 mm Nb-filter), (c) Estimation of shooting distance according to measured Pb impulse rate (circular area around entrance hole: 34 mm diameter), and (d) Radial Pb-distribution around the bullet hole in dependence of the shooting distance.

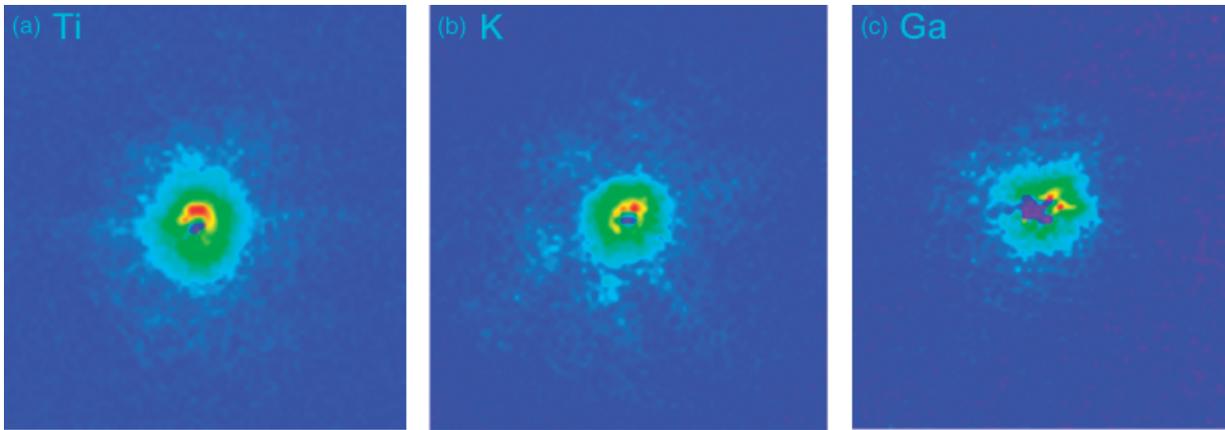


FIG. 5—Elemental distribution of (a) Ti (“Action 4”—RUAG), (b) K (“Nontox”—S&B), and (c) Ga (“QD-PEP II/s”—MEN) originating from different lead-free ammunitions that are not detectable by common chemographic methods (collimator: 2 mm Nb-filter, shooting distance: 5 cm).

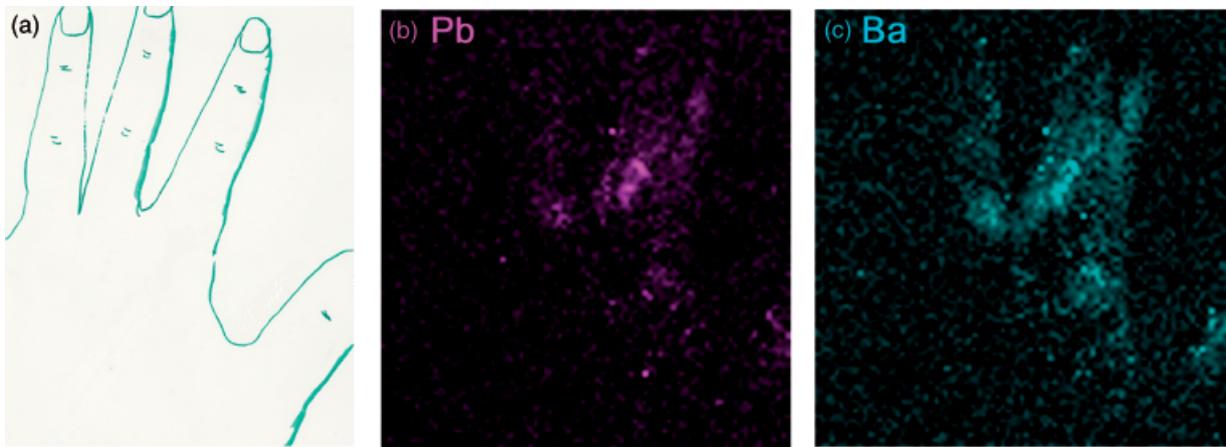


FIG. 6—Adhesive tape lift of a shooter's hand and corresponding elemental mappings of Pb and Ba (collimator: 2 mm Nb-filter) clearly indicating the outlines of the hand—(a) overview: adhesive tape lift of shooter's hand, (b) X-ray fluorescence analysis (XRF) mapping of Pb on adhesive tape, and (c) XRF mapping of Ba on adhesive tape.

K as a detectable metallic component in the primer can be identified using the *Midex M*.

All investigations described so far were performed using cotton fabric as a target material for the test shots. The m-XRF measurements were directly carried out on the fabric. But, as mentioned before, other substrate materials are also suitable for *Midex M* investigations. An important example is adhesive tapes (e.g., Filmolux[®] films) (8,9). They help to avoid a limitation of the spectrometer: as the ideal working distance is 2–3 mm, the method

is limited to the examination of flat specimens only. As many objects of interest do not fulfill this requirement or are too large for the sample chamber, the commonly applied tape-lift method using thin adhesive tapes to collect GSR-particles offers a promising alternative. The GSRs are transferred onto the secondary target accessible for the m-XRF examination by using the same specimen holder as applied to fabrics evidence.

An example of this special application is the investigation of GSR of shooters' hands by transferring GSR to a Filmolux[®] film

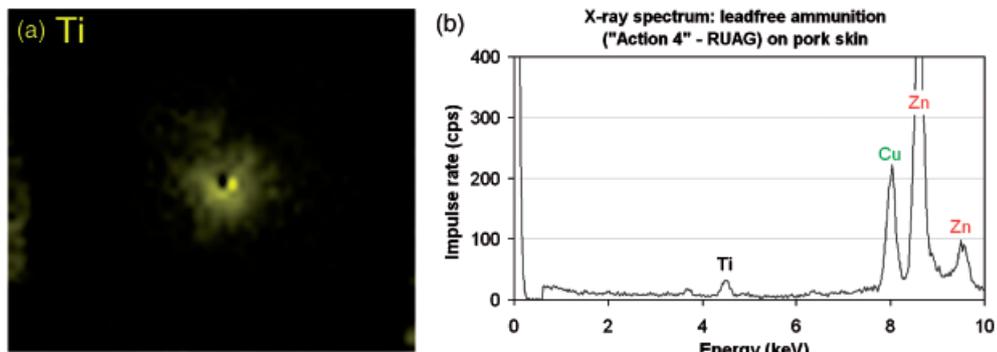


FIG. 7—Gunshot residue (GSR) of nontoxic ammunition (“Action 4”—RUAG) on pork skin—(a) X-ray fluorescence analysis mapping of the elemental distribution of Ti, mapping size: $\sim 10 \times 8$ cm, and (b) point scan to identify the composition of the GSR (collimator: 2 mm Nb-filter, shooting distance: 5 cm).

(Fig. 6a), as is widely used in Germany and other European countries within chemographic investigation (2). The elemental mapping of Pb (Fig. 6b) shows the distribution of Pb-containing particles on the hand and their aggregation around the forefinger. A comparable elemental distribution was found for Ba (Fig. 6c) and Sb (not shown), as expected.

Investigation of GSR Patterns on Tissue

The investigation of GSR on tissue is often difficult. Such examinations need a reliable and durable cooling to minimize the decomposition of the tissue during measurement time and to reduce odor effects as well. Therefore, pork skin was investigated, shot at from a distance of 5 cm with a Sintox primer ammunition ("Action 4"—RUAG). Figure 7 shows the elemental distribution of Ti recorded by m-XRF mapping. These results can be applied to human tissues, and comparative studies for forensic applications are possible. Misidentification of elements due to overlapping effects (e.g., Ti K_{α} and Ba L_{α}) can be eliminated by the possibility of choosing the intensities of a whole series of an element for the evaluation and not only the K_{α} intensity.

Conclusions

The *Spectro Midex M* has proven to be a versatile tool for GSR analysis in general as well as for shooting range estimations. This method will not replace other common techniques in GSR investigations but is a good supplement, especially with nontoxic primers becoming more and more popular. The following list summarizes the advantages of the m-XRF method in brief:

- nondestructive method;
- the large motorized stage allows the use of special specimen holders designed for various types of samples;
- quick survey of GSR-related elements in point scan and line scan modes;
- mapping of large surfaces (up to c. 20 × 20 cm) within acceptable measurement times of 3–4 h without the need of cutting out regions of interest;

- access to GSR distributions of any element accessible for XRF methods (no need for suitable coloring reagents, which are difficult to find for elements used especially in modern nontoxic ammunition);
- additional data processing is possible to evaluate (semi)quantitative information on the elements present; and
- the tape lift technique allows the investigation of samples that are too large for the sample chamber or not planar by transferring the GSR particles to adhesive tapes.

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