Combining grazing incidence X-rays and micro-diffraction for qualitative phase identification in forensic powdered micro-samples

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Abstract

Capillary diffraction or microdiffraction are standard techniques for characterizing small samples when only a few milligrams are available. On the other hand, we have typical grazing incidence diffraction or different variations of grazing incidence (GI) diffraction used, such as in-plane grazing incidence (IP-GI) or GI using a micro focusing source, to study thin films. However, when few powder micrograms are available, the characterization task is complicated. In the present work, few micrograms of typical forensic samples are analyzed using standard Bragg-Brentano, X-ray powder diffraction geometry, and grazing incidence X-ray micro-diffraction (GIμXRD). Samples include soils, cosmetic eyeshadows, two different pyrotechnic mate

rials, and a highly explosive mixture contained at primer cup of ammunition. The analysis was carried out from 1 to 5 degrees of the incident parallel beam with a shaking sample. Depending on the fixed incident angle, different small regions of the diffraction patterns showed an improvement in the intensity of the peaks with respect to the conventional Bragg-Brentano configuration. However, 3–5 degrees of the fixed incident beam showed the best results. This new data acquisition technique, based on the combination of two known diffraction methods, could be a powerful tool for studying samples outside of forensic sciences such as nanomaterials, medicine, or any other field where the sample quantity is extremely small, also, without the need to transport evidence and travel to external facilities with higher analytical performance such as synchrotron radiation installations or other large experimental facilities.

Keywords: X-ray diffraction, Bragg-Brentano configuration, Grazing Incidence, micro-diffraction, forensic samples, irradiation angle.

1. Introduction

X-ray diffraction is probably the most used standard technique for determining the crystallographic structure of any material. X-ray radiation interacts with the material electrons provoking the process of scattering and due to the order in the crystal, the promotion of diffraction phenomenon. For thin films research, the used wavelength radiation can be a problem due to the high penetration inside the sample, and therefore unique geometries are necessary to profit from such penetration and maximize the diffraction signal concerning the diffraction bulk, even if the substrate bulk is a glass [1]. Marra et al. used for the first time a grazing incident angle of the impinging X-ray beam to study the structural properties of the GaAs-Al semiconductor thus enhancing the surface signal on the diffraction pattern (experimental setup called grazing incidence X-ray diffraction, GIXRD) [2]. The proposed technique resulted in a powerful tool to study ordered interfaces, epitaxial heterostructures, multilayers and surface phenomena, by limiting/controlling the X-rays' penetration into the bulk. Nowadays, different geometries of GIXRD are performed to study the crystallographic orientation, lattice mismatch, order parameter, and phase of in-plane reflection for various thin-film systems [3]. Nowadays exist some variations for coplanar and in-plane grazing incidence using single multilayer mirror, polycapillary optics or even microfocusing in the primary beam [4]

On the other hand, another relatively new analysis technique of X-ray diffraction is the micro X-ray diffraction (μXRD) analysis. In general, micro-diffraction is a term which covers many diffraction analysis involving small samples or small area or small volume of a large sample [5]. Indeed, X-ray micro-diffraction is a combination of the standard X-ray diffraction and X-ray focusing optics to improve spatial resolution [6]. Here, a very narrow beam of highly **focalized** X-rays is used to measure tiny areas of around 50 μm^2 or smaller. This technique is broadly used in a small or non-homogenous sample with varying composition, including contaminants or inclusions [7], and also has been used to create maps of strain/stress in thin films [8]. This technique is applied to many diffraction investigations in different fields such as mineralogy, archeological samples, paintings, or forensic samples [9]. Furthermore, X-ray micro-diffraction has proved to help for tissue-engineered bones and **to** understand the biological process involved [10].

Forensic samples and samples from artworks are heterogeneous, unique, and unrepeatable due to the limited sampling or their use as evidence in a court trial [11]. Therefore, it is extremely important to avoid any destructive analysis method to obtain maximum information without losing material or to minimize pre-treatments to examine the samples. Soil samples, eyes shadow, pyrotechnic materials, and gunshot primer are routine forensic samples found in a crime scene as traces evidence. It is then necessary to identify them categorically without destroying or changing the sample by the use of non-destructive analytical tools, such as scanning electron microscopy and energy dispersive X-rays analysis (SEM-EDX), X-ray diffraction (XRD), or X-ray fluorescence (XRF). EDX and XRF are elemental analysis techniques, and XRD is used **for the** phase identification of crystalline or semi-crystalline samples. When the different techniques are used together, a robust study is obtained. However, even when in EDX, minimal quantities of sample are enough for the

analysis, **due to the reduced analytical small spot, around few microns**; in conventional XRD, it is a different situation, and usually, few milligrams are used to obtained reliable results [12]. Even more, by XRD it is possible to study at the same time organic and inorganic samples while by the use of other techniques, such as ionic chromatography or gas chromatography with mass spectroscopy, it is necessary to separate the different organic or inorganic phases [13].

In this work, we tested forensic samples by a combination of grazing incidence X-ray diffraction and X-ray micro-diffraction (GIμXRD) using an advanced Empyrean diffractometer instrumentation (Malvern Panalytical Ltd.) able to operate in many different experimental setups. Therefore, we can compare our results of GIμXRD, with those obtained by using conventional Bragg-Brentano XRD.

2. Experimental

2.1 Instrumentation

The samples were examined with the use of an environmental scanning electron microscope, ESEM Quanta 3D 200i (FEI Inc., Hillsboro USA, now owned by Thermo Fisher Scientific), coupled with an Energy Dispersive X-ray spectrometer, (EDAX Inc., Ametek LLC) with a 30-mm^2 silicon drift EDS detector for determining elemental composition (resolution 129 eV for Mn Kα at intensity of 10000 cps). The acceleration voltage was 25 kV, and the working distance was 15 mm.

X-ray powder Grazing Incidence micro-diffraction experiments and conventional Bragg-Brentano data of all experiments were collected with an Empyrean diffractometer (Malvern Panalytical Ltd.) equipped with a copper X-ray-tube (K_α wavelength 1.5406 Å) at 45 kV and 40 mA with a step size of 0.013° and time per step of 198.6 s. The used detector was a 2D solid-state hybrid pixel detector Pixcel 3D. We used linear focus with incident configuration optics for conventional Bragg-Brentano configuration: soller slit of 0.04 rad and automatic divergence slit irradiating a constant length of 10 mm, fixed divergence slit of 1. We used an automatic anti-scatter slit (10 mm), a soller slit of 0.04 rad, and a Ni filter on the diffracted side. For the GIμXRD measurements, we used a point focus mode of the incident beam with a mono capillary (0.3 mm) to generate a pencil beam. On the diffracted side, the optics were the same as in the case of Bragg-Brentano.

2.2 Samples

Soils and eyes shadow samples were study materials of ongoing projects of the Laboratory of Analytical X-ray Applications (IDAEA / CSIC, Spanish Council for Scientific Research, Barcelona, Spain).

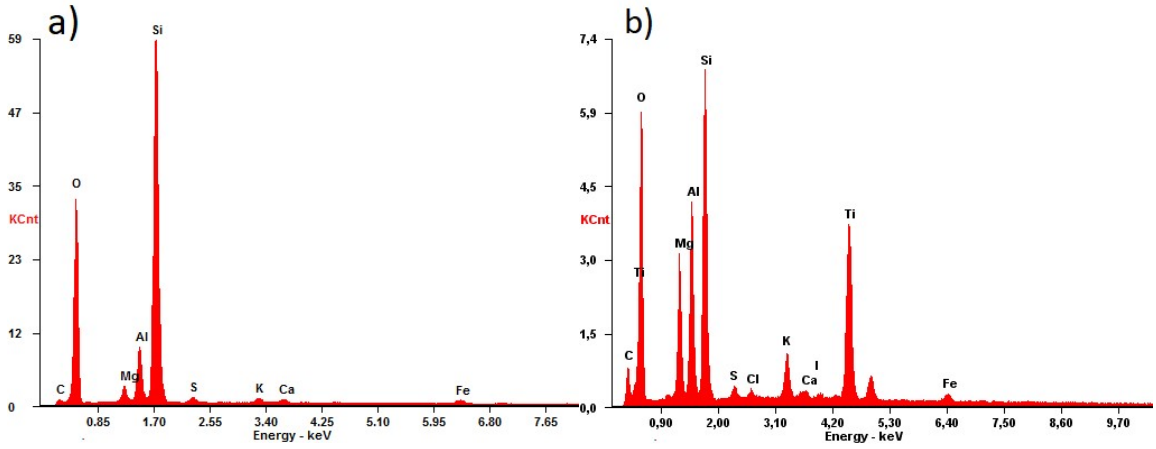
The pyrotechnic materials were acquired from distribution companies in Puebla-México. The white pyrotechnic material is used **for the so called "palomas" explosive (see description in https://aztecakgames.fandom.com/es/wiki/Palomas_explosivas)** and the **black gunpowder used for the pyrotechnic "Rockets" products**.

Finally, under the Ballistic Laboratory's supervision, three rounds of ammunition of 9 mm Luger (CBC, Companhia Brasileira de Cartuchos) were disassembled using a Kinetic Bullet Puller to dislodge the bullet from the shell casing. With the bullet out of the way, all propellant (smokeless powder) was removed from each casing leaving only the intact sealed primer cup. The explosive mixture contained in the primer cup was extracted and stored for later analysis.

For the conventional Bragg-Brentano configuration, we used 30 mg of the sample, and for GIμXRD less than 10 μg arranged in a 3-4 mm line, and with shaking system. Glass slides were used as sample holders.

3. Results and discussion

When unknown samples are analyzed, it is always important to use different characterization techniques to study the presence of different elements and, therefore, strengthen the samples' analysis. The elemental analysis was done by Energy Dispersive X-ray Analysis (EDX). Figure 1 shows the EDX analysis for the different samples studied in this work.



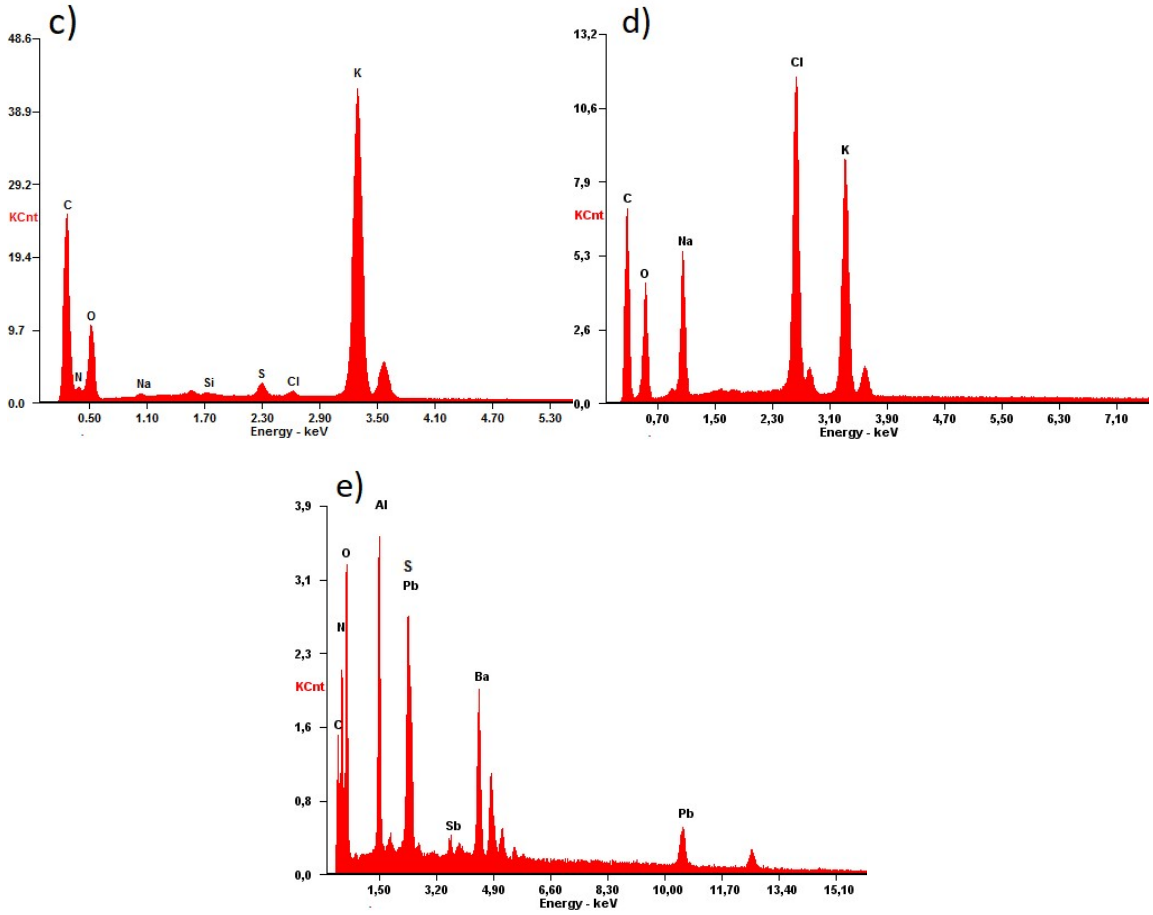


Figure 1. EDX spectra of the samples a) soil sample, b) eyes shadow, c) black pyrotechnic material, d) white pyrotechnic material, and e) priming compound (explosive mixture) contained at primer cup.

The observed elements were used to help the identification of the compound phases in GIμXRD plots of the different forensic samples. The presence of compounds was checked using the Powder Diffraction File PDF-4™ database from the International Center for Diffraction Data (ICDD, Newton Square, PA, USA).

Figure 2 shows the XRD pattern in the conventional Bragg-Brentano configuration for 30 mg and 8 µg of the different samples. In general, the samples with a few micrograms does not show intense enough peaks to identify all the phases. In particular, and depending on each material's crystallinity, Figure 2 b and c (eyes shadow and black pyrotechnic material) do not show any clear peak when few micrograms are analyzed. For the 30 mg samples, it was possible to identify four phases for the soil sample (Figure 2a): palygorskite $Mg_5H_{18}O_{30}Si_8$ (PDF 021-0957), kaolinite $Al_2H_4O_5Si_2$ (PDF 001-0527), alunite $Al_3H_6KO_{14}S_2$ (PDF 072-1630) and quartz SiO_2 (PDF 075-0443).

In the case of the eyes shadow (Figure 2b), it was possible to identify 6 different phases: anatase TiO_2 (PDF 01-071-1166), talc 2M $Mg_3Si_4O_{10}(OH)_2$ (PDF 00-019-0770), silica SiO_2

(PDF 01-073-3446), Mica $KMgAlFe_{2.3}O_{13.7}•86H_2O$ (PDF 00-002-0044), chlorite/serpentine $(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$ (PDF 00-052-1044), and dolomite $CaMg(CO_3)_2$ (PDF 01-081-8225). For the black pyrotechnic material (Figure 2c), we identified three phases: potassium nitrate KNO_3 (PDF 04-009-1184), potassium sulfate K_2SO_4 (PDF 00-005-0613), and sodium nitrate $NaNO_3$ (PDF 00-047-0380). For white pyrotechnic material (Figure 2d), three different phases were identified: Sodium Benzoate $C_7H_5NaO_2$ (PDF 00-005-0053), potassium chlorate $KClO_3$ (PDF 014-0544), and potassium perchlorate $KClO_4$ (PDF 007-0211).

Finally, for the priming compound (explosive mixture in Figure 2e), five phases were identified: antimony sulfide Sb_2S_3 (PDF 00-042-1393), Lead styphnate $C_6H_3N_3O_9Pb$ (PDF 00-044-1624), barium nitrate $Ba(NO_3)_2$ (PDF 01-076-0920), Aluminum Al (PDF 01-089-2837), and some small traces of lead styphnate hydrate $C_6HN_3O_8Pb•H_2O$ (PDF 00-040-1745).

Considering that the available samples found in a crime scene are minimal, 8 μg of the different samples were measured by the conventional Bragg-Brentano (B-B) configuration and by GIμXRD configuration at different incident angles (1 to 5 degrees), **as it could be** shown in Figure 3. As in Figure 2, it can be observed that in the B-B configuration, the peaks are not intense enough to index the different involved phases for each sample. Just a few small peaks are appreciated but depend again on each sample. One and two degrees of incidence radiation are not, in general, a good option. Here, not all the peaks corresponding to all the present phases are observed (Figure 3 a, b, d, and e), or the peaks are agglomerated in a broad and not defined peak as in Figure 2c. However, when GIμXRD configuration is performed at angles 3-5, all peaks' intensity and sharpness are increased sufficiently to differentiate them from the background or other peaks.

For the sample of black pyrotechnic material (Figure 3c), the irradiation at 3 degrees still provokes the broadening and agglomeration of peaks (see the region around 43° in 2θ angle). In this particular case, 4 and 5° are the best irradiation angle option, even when we found that the intensity of those peaks above 40 degrees is enhanced even from 2° irradiation angle. In general, due to the few micrograms **available, and assuming a limited number of crystalline grains causing the counting statistics signal** in the whole X-ray diffraction patterns, **we can expect very different** behaviors depending on the crystallinity of each sample.

For example, in Figure 3a, the patterns for all **incident** angles of **X-ray beam** are similar, they just increased or decreased the peaks intensity in different regions when the angle change. In Figure 3c, at one and two degrees of the fixed incident radiation there are a couple of broad peaks above two theta 20 degrees that disappear for higher incident angles. In Figure 3 b, d and e, some peaks appear and disappear at different incident angle. **However,** all the observed peaks in all diffraction patters correspond to the identified peaks observed for the bulk materials, indicating that the used of GIμXRD applied in powder minimal samples can be an excellent option to their characterization.

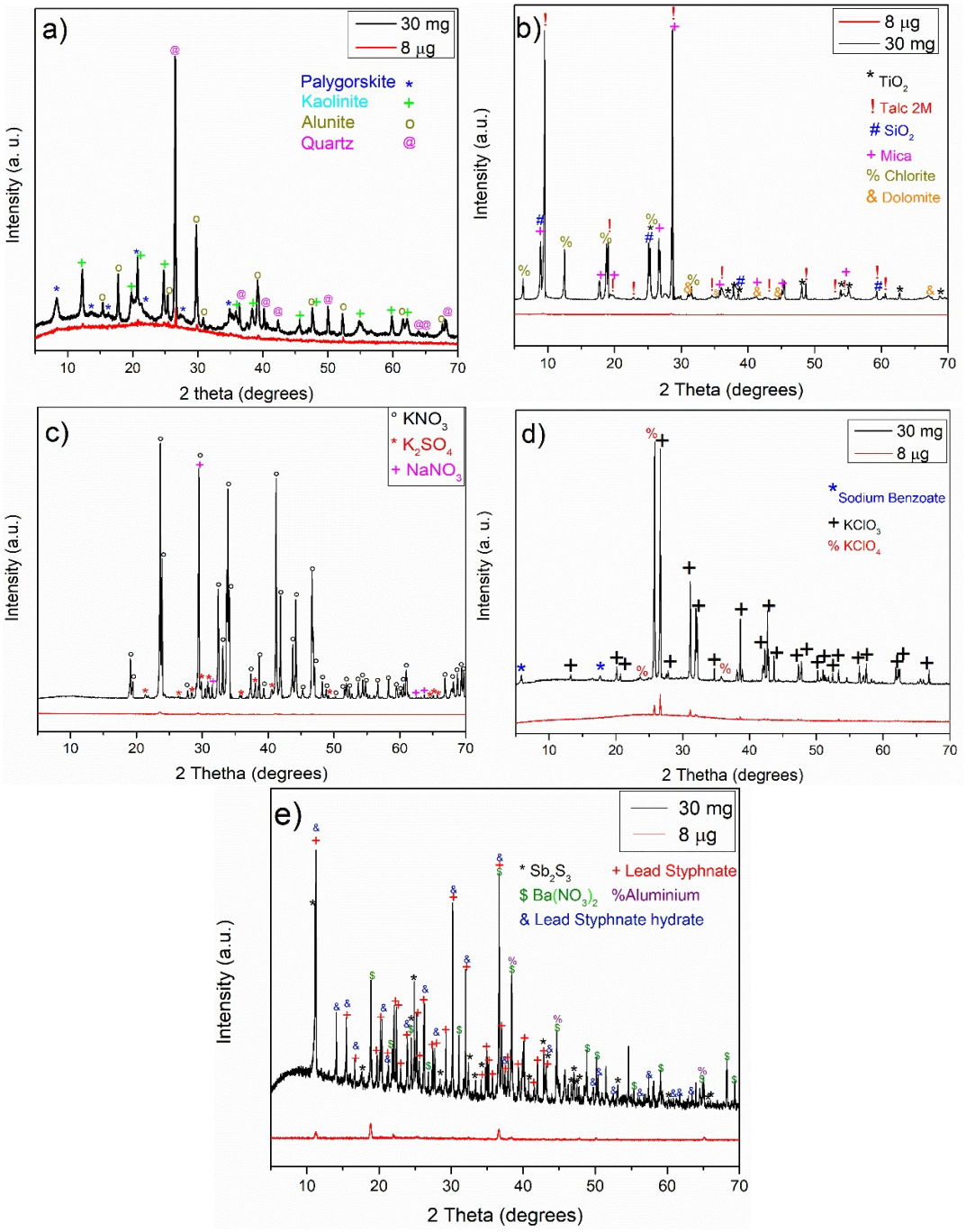


Figure 2. XRD powder patterns of 30 mg and 8 µg of the a) soil sample, b) eyes shadow, c) black pyrotechnic material, and d) withe pyrotechnic material, and e) priming compound (high explosive mixture), in Bragg-Brentano conventional configuration.

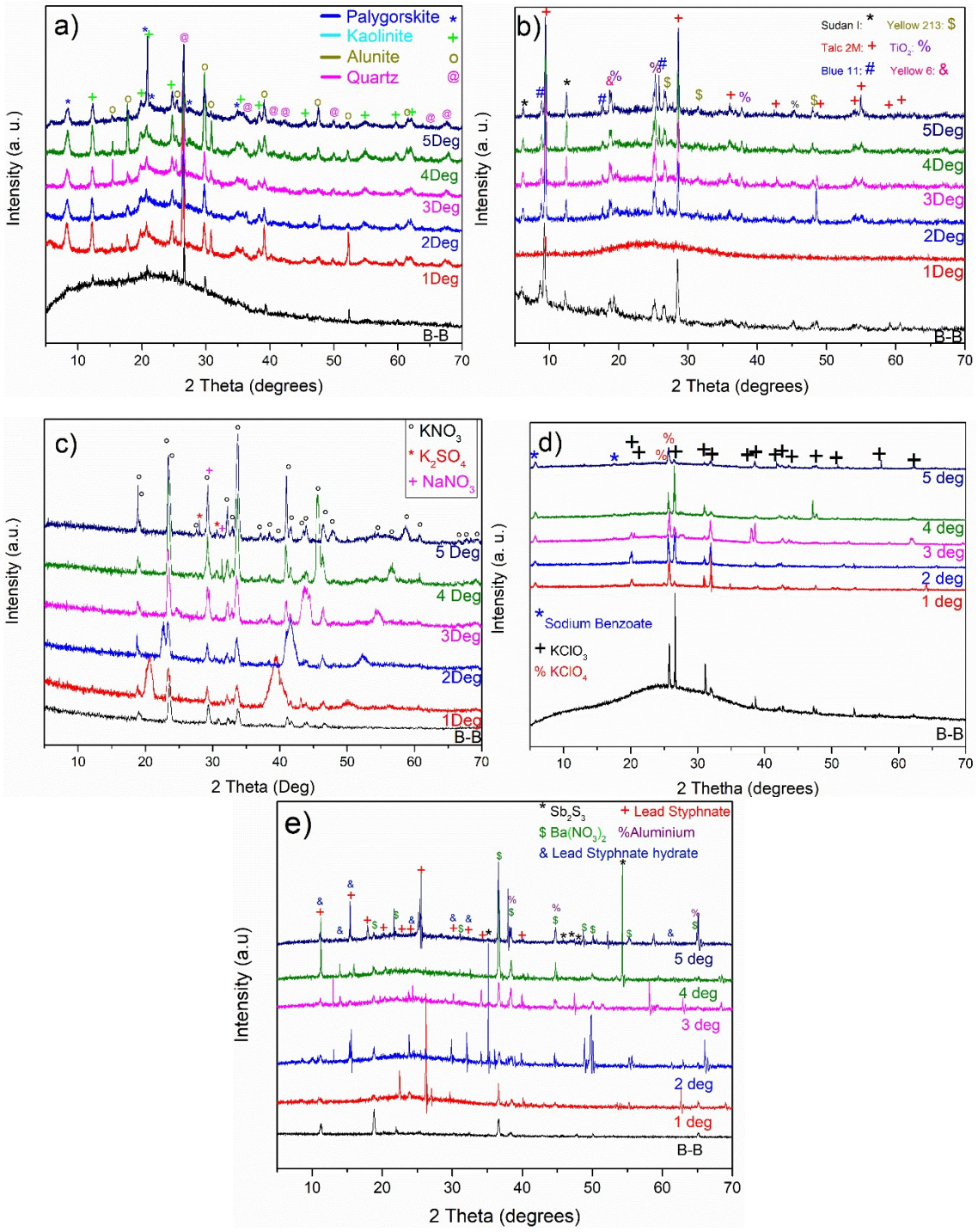


Figure 3. Powder patterns of 8 µg of the a) soil sample, b) eyes shadow, c) black pyrotechnic material, d) white pyrotechnic material, and e) priming compound (high explosive mixture), measured with the conventional Bragg-samples, and different angles of fixed incident angle.

Low angles of the fixed incident X-ray beam have been previously used in forensic sciences to study a bullet shot fired through zinc-plated steel and a duralumin sheet [7]. They just used the low fix angle (5 degrees) to suppress the X-ray beam's penetration depth and enhance the signal of the studied layers. However, as far as we know, it has not been used to study powders by varying the incident angle to improve the diffracted signal from the entire diffraction pattern when very few powder micro-grams should be analyzed.

Our simple study using a laboratory diffractometer device with a simple geometry shows a powerful tool to study samples when few micrograms are available.

4. Conclusions

Application of a combination between grazing incidence X-ray diffraction and micro-diffraction was performed to analyze few micrograms of different forensic samples. It was shown that GIμXRD is not only useful to suppress the penetration deep of X-ray beam and avoid signals from the substrate when used in films, it is also beneficial to observe diffracted signals from minimal quantities of powders. Furthermore, the angle variations allow enhancing the intensity at different angles in 2 theta of the pattern. Nevertheless, the best results are obtained when using 3 to 5° of the fixed incident angle. This **combined** technique could be promising to analyze a variety of tiny samples in arts, medicine, nanomaterials, and especially in forensic science, where evidences at crime scenes have a great diversity of matrices and complex samples.

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Conflict of interest

Authors declare no conflict of interest

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