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Modular MA-XRF scanner potentialities and further advances

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***Abstract* – In Heritage Science applications, *in-situ* and non-destructive analyses are commonly preferred. The valuable nature of historical objects often hinders the possibility of either sample or transport them into laboratories. Macro X-ray fluorescence (MA-XRF) has become widespread in the archaeometry field, due to its non-destructive and non-invasive characteristics and especially to the amount of information provided by the technique. Unfortunately, most of the instruments are either fixed or mobile, hindering their *in-situ* applications. Moreover, most of the mobile instrumentation are bulky and require some logistics for transportation. In this scope, a modular instrument has been developed. The scanner, which requires no more than one person to transport and assemble, has been tested and compared under compatible circumstances to state-of-the-art instrumentation. Preliminary results are presented and discussed.**

I. INTRODUCTION

Energy-dispersive X-ray fluorescence (ED-XRF) is a well-known and consolidated technique that has been used for decades to study a wide variety of materials [1][2]. More recently, it started being used in a 2D fashion, producing elemental distribution maps that allow a spatial visualization of chemical species [3][4][5].

The development of portable and mobile instrumentation has been in the spotlight for a considerable time, especially given the nature of heritage materials, which can be rarely transported into laboratories or synchrotron facilities [6]. Commercial and *in-house* developed macro-XRF scanners are now readily available, with only a few of the in-house systems being portable. Portability comes at the cost of smaller scanning areas, limiting its application on larger samples (as paintings). On the other hand, portability can be a critical factor in a research field where sample displacement is hindered [6][7].

In what regards resolution, X-rays focusing optics are generally used, focusing the beam up to few dozen micrometres [8]. Such small beam sizes can be achieved with polycapillary lenses. However, they reduce the beam overall intensity, requiring powerful sources (10W +) to obtain quality spectra at short dwell-times. Alternative focusing optics are pinhole collimators, where the focused beam is usually larger (0.5 – 2 mm) but provides an almost constant size across the z-axis and less energic losses in respect to polycapillary lenses [9].

When it comes to pricing, most of the system's cost is related to the X-rays electronics. This cost can be reduced if low-power electronics and simple focusing optics are used, with the drawback resulting in larger dwell-times and lower resolutions. As system portability and maximum scanning area are competing parameters, difficult choices, apart from budget, must be made when considering developing one single scanning system, sacrificing either one or another parameter.

In this scope, combining cost-effectiveness and versatility, a modular scanning unit was developed in a joint effort between Ars Mensurae, Istituto Nazionale di Fisica Nucleare – Roma TRE and Sapienza University. The translation stages and scanning head were designed as independent modules, the latter featuring exchangeable electronics (X-ray tube, optics, detector(s), and distance sensors). In this way, the system can adapt to different situations, following a *plug-and-play* approach.

The instrument described has been previously tested on several types of materials of cultural heritage interest [10][11]. Nonetheless, it has not been yet tested with ceramic materials or directly compared with state-of-the-art instrumentation. Therefore, in this work, a Portuguese *azulejo* from the XVII century was scanned with both the *in-house* developed instrument and a commercial one to assess the former instrument's efficiency and performance. Comparisons between the instruments are presented and few results and potentialities of the modular scanner discussed.

II. METHODOLOGY

A. Scanning system

To overcome one of the major disadvantages of portable systems, two scanning stages were developed, one being small and portable, capable of scanning areas up to 20×20 cm^2, and a larger one, capable of covering areas up to one square metre.

Multiple X-rays detectors can be fitted in the scanning head to reach shorter dwell-times if needed. The X-ray tube can be exchanged, as the head threading can fit any of Moxtek's® *analog-handheld* tubes. The beam is focused with an exchangeable aluminium collimator. The current prototype iteration uses up to 3 AMPTEK® X-123 SDD detectors, which are low power and lightweight. The detectors are configured identically, so acquisition can be synchronized and the sum spectrum from all detectors viewed in live time.

In addition to the X-rays electronics, the x-y scanning stage can be exchanged as well. This allows one to achieve quick assembly times (ca. 25 min) as well as provides an extra degree of versatility. X-rays detectors and scanning stage(s) are controlled by the same acquisition software, developed in the LabVIEW® platform. The tube is controlled externally, not integrated in the controlling software, enforcing the system's modularity.

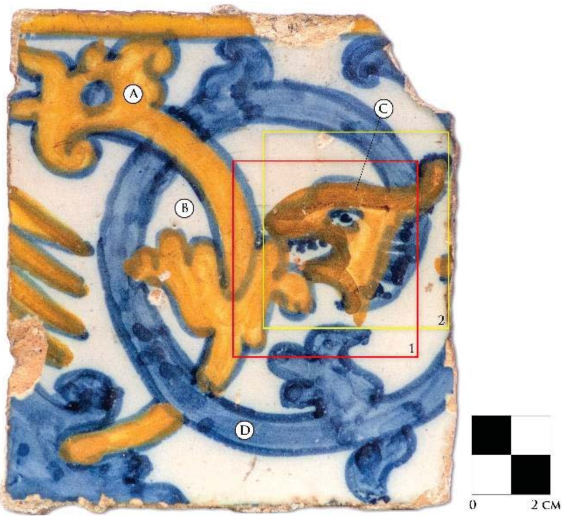

Fig. 1. Sample and scanned areas, (1) modular scanner, (2) M4 Tornado. The colours identified are: (A) yellow, (B) white glaze, (C) orange and (D) blue.

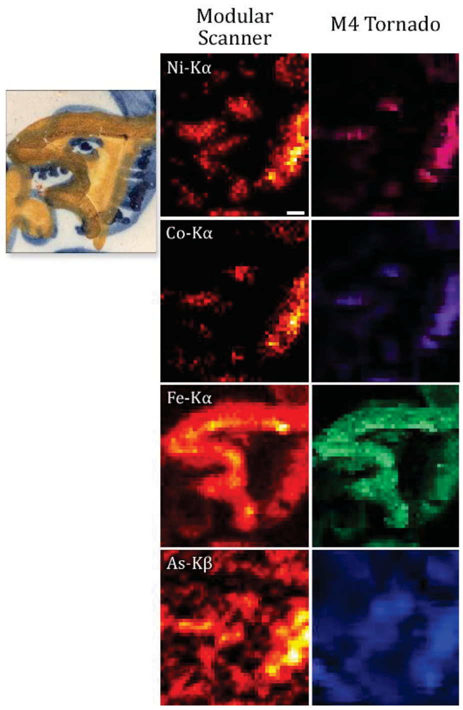

Fig. 2. Elemental distribution maps for nickel, cobalt, iron, and arsenic. Scale bar dimension is 5 mm.

In sum, the system can be configured to suit each necessity. The scanning head (with only one detector), cables, small stage and all related peripherals can comfortably fit inside a standard airplane cabin trolley. The portable version is described in more detail elsewhere [12].

B. Materials

To test the system and compare its performance with state-of-the-art instrumentation, one Portuguese *azulejo* (probably from the XVII century) was chosen and had one small portion scanned with both instruments.

The sample presents typical colours found in similar *azulejos* from the same period, but with a rather poorer palette, presenting less colour variety. In the palette, three main colours can be identified apart from the white glaze: blue, yellow, and orange (**Figure 1**). Colours which are also typically found in *majolica* tiles [13].

C. Data acquisition

The areas scanned by both the modular scanner and the M4 Tornado are highlighted in **Figure 1**. Albeit M4 Tornado can provide considerably shorter dwell-times, thanks to its high-power tube, both analyses were performed under the most similar conditions possible, to ascertain the results are comparable. Scanned areas were 5.3×5.0 cm^2 in size each and were acquired with a 35 kV voltage and 29 µA current. Dwell-times were set to 500 ms

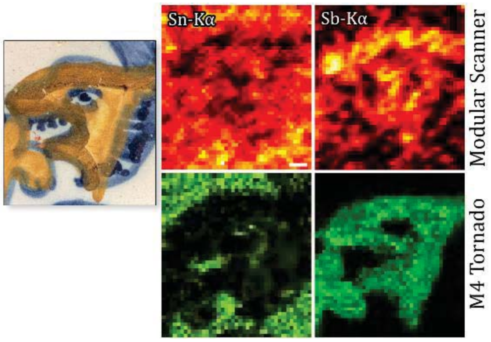

Fig. 3. Elemental distribution maps for tin and antimony. Scale bar dimension is 5 mm.

for the M4 Tornado and 470 ms for the modular scanner, with an overall stage speed of approximately 2 mm/s. The M4 Tornado scanner is equipped with a Rh target X-ray tube, while the modular scanner had an Ag target Moxtek® tube attached. The modular scanner was assembled with the larger stage and one X-123 SDD AMPTEK® detector.

Overall scanning time was about 20 minutes for each instrument. Elemental distribution maps were generated by different software. M4 Tornado images were obtained with Bruker ESPRIT proprietary software. Data obtained with the modular scanner was processed with an *in-house* developed software (XISMuS) version 1.0.1dev [14].

III. RESULTS

A. Scanners performance

A comparison between the major elements' distribution images obtained with both instruments is shown in **Figure 2**. The images presented little to no difference, except for the arsenic maps. The advantages provided by a smaller beam size, at the given analysis conditions, were not fully explored and therefore, not appreciated. For larger and faster scans, where the beam size if often wider (≈ 1 mm), the costs trade-off between having an instrument with polycapillary lenses and choosing collimator optics can therefore be justified.

Figure 3 shows a comparison between antimony and tin maps. These maps, obtained from their respective elements K-lines, presented significant differences in image quality and resolution. These fluorescence lines are highly energic and the peak shape appears broader in the dataset obtained with the modular scanner (**Fig. 4**). With the current conditions, M4 Tornado detector performed better in the high-energy end of the spectrum. It is important to highlight that the AMPTEK® detector worked with 1024 channels while M4 Tornado detector worked with 4096 channels; that being rather a settings restriction for the former instrument.

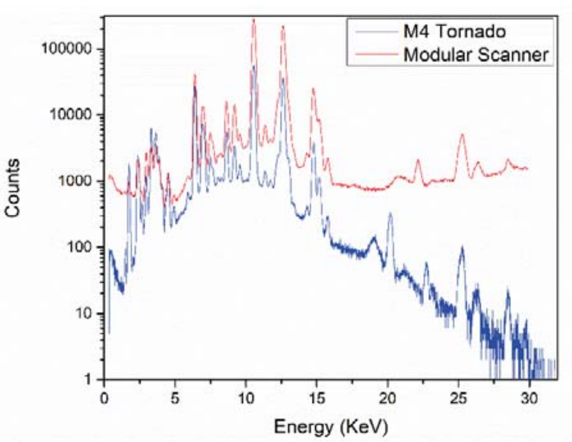

Fig. 4. Sum spectra of scanned regions.

B. Analytical results

The modular scanner's cobalt map (**Fig. 2**) was obtained by subtracting the iron map from it, due to a high peak overlapping between these two elements. The blue pigment and its hues present a combination of cobalt, iron, and nickel. Iron, nonetheless, can be appreciated in much higher quantities correlated to antimony, in the orange pigment region. Arsenic was detected in correspondence with the previous three elements within the blue region. This quaternary combination can be directly related to *zaffre*, imported by Portugal from Germany in the beginning of the XVI century [13]. Nonetheless, the blue pigment origin must be treated with caution, as there are few other documented cobalt sources available for this period, as Spain for instance. A local production of cobalt blue is known to have been stablished in Portugal in the first quarter of the XVI century, due to the elevated price of the pigment [13][15].

In **Figure 5,** few more element distribution maps can be appreciated, from which it is possible to better understand the yellow pigment's nature. This pigment can be clearly characterized by the concomitant use of lead, antimony, and zinc. Tin can be found in lower quantities, but its signal is much more appreciated in the white glaze, which in turn is known to be commonly made of lead and tin oxides (usually cassiterite and PbO). Even though calcium is detected in what seems to be a correlation, its presence is hardly associated to any of the pigments. Majolica plates from the XVI century had the Pb-Sb-Zn triple yellow detected, in what is usually referred to as an orange-yellow [16].

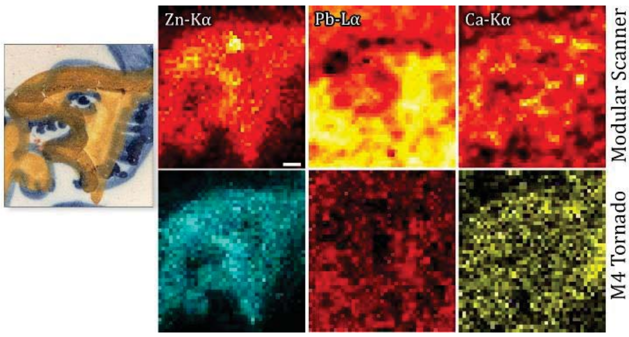

Fig. 5. Elemental distribution maps for zinc, lead, and calcium. Scale bar dimension is 5 mm.

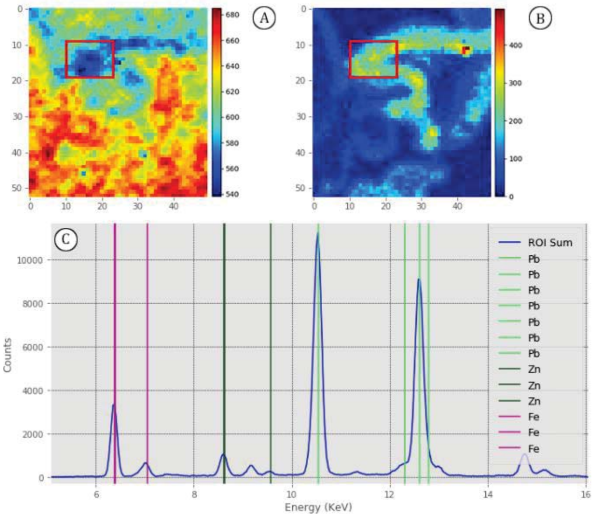

Fig. 6. Sum spectra of a selected subregion (C). Maps depicted: lead-Lα (A) and iron-Kα (B). Scales represents counts.

The *azulejo*'s orange pigment is rough to the touch and seems, at first, to be a combination of iron, antimony, and zinc. Lead can be detected in the orange region, but its signal is likely to come from the glaze instead (**Figure 6**). This pigment has been reported to be a mixture of yellow pigment with iron oxide [13].

IV. CONCLUSIONS

A direct comparison between a state-of-the-art scanner and an *in-house* developed modular scanner was made. The modular scanner has clear advantages when it comes to mobility and flexibility. It is modular and cost-effective, being able to scans areas up to 1 m^2 and transported easily. The images output, in the given analytical conditions, were very similar, with exception to maps from the higher energy end of the spectrum.

A preliminary evaluation of the *azulejo* pigments was pursued. Results obtained with the modular scanner were mostly in accordance with similar artifacts from the same period. The yellow pigment demonstrated to be a combination of Pb-Sb-Zn, identified in XVI century majolica. The orange pigment presented a rather different composition from other similar samples, apparently devoid of lead and tin. These elements are, instead, more likely to be present in the white glaze, which can be rather thick (200-500 μm) [13]. The blue pigment detected is the traditional cobalt-based blue, commonly found in many Portuguese *azulejos*, and composed of a quaternary combination of Ni-Co-Fe-As.

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