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Characterization of the new mobile confocal micro X-ray fluorescence (CXRF) system for *in situ* non-destructive cultural heritage analysis at the CNA: μXRF-CONCHA☆

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ABSTRACT

Confocal micro X-ray fluorescence (CXRF) is gaining considerable interest due to its ability to provide compositional and spatial information that are typically obtained using standard micro-invasive and/or micro-destructive techniques (e.g., SEM-EDX), without the need of sampling. In this work, the specifics of the new CXRF device named μXRF-CONCHA from the *Centro Nacional de Aceleradores* of the University of Seville will be presented. The development of this equipment is intended to the study *in situ* of paintings in order to obtain depth profiles of pictorial layers by a no-destructive way. This investigation consists in studying the viability of this device for the study of pictorial layers of old paintings. The challenge consists in determining if the results obtained allow distinguishing the sequence of the paint layer and their composition. Several experimental paint multilayers have been analyzed to evaluate this setup. This paper shows that μXRF-CONCHA will be able to provide important information in order to understand and interpret the choice, palette, and technique of painters from the past.

1. Introduction

Through the years, the importance of the development of non-invasive and non-destructive new techniques for the study of cultural and historic heritage and the mobility of those techniques applied for analysis *in situ* are still increasing. The design of a mobile equipment of confocal micro X-ray fluorescence(CXRF) corresponds to this needs in the way to obtain a quality of information similar to other well established micro-invasive and/or micro-destructive techniques (as analyses of micro-samples by scanning electron microscope) without the necessity to intervene on the analyzed object [1].

In the last decades, CXRF extended the potential of the technique known as micro X-ray fluorescence (μ-XRF) to depth profile of multilayer materials [2–5]. The μ-XRF technique consists of the placement of a polycapillary X-ray lens at the exit of micro-focus X-ray tube, with 45° between the excitation and detection channels and 90° between the excitation channel and the surface of the sample (Fig. 1). Meanwhile, in CXRF, an additional polycapillary lens at the entrance of the X-ray detector is employed to limit the space from which X-ray photons can be detected (Fig. 1) [6]. In the case of CXRF, the excitation channel forms an angle of 45° with respect to the surface of the irradiated object and 90° with respect to the detector channel [7].

Confocal micro-X-ray fluorescence is a non-destructive technique that can provide depth-resolved information about elemental composition and it has proven its suitability in the investigation of stratified structures in microscales [8–11]. A probing micro-volume (called confocal volume) is defined by the overlap of the foci of both X-ray lenses [12]. By scanning materials through this micro-volume, one can obtain intensity profiles reflecting the local elemental composition variation versus depth or versus a lateral coordinate (with a resolution in the range of 3 to 10 μm for most CXRF setups) [1]. The maximum depth of analysis is limited by absorption effects and usually does not exceed 1 mm in low-Z matrices or tens of microns in heavy-Z matrices.

CXRF is a relatively novel technique and may appear under different names in scientific publications. This fact may difficult the visibility of the technique. Sometimes, the name used focuses on the 3D ability of the technique for example “3D micro-X-ray fluorescence” [5] or “confocal 3D XRF” [13]. Acronyms such as 3D-XRF will not be used in this work as it results in a misuse of language. On one hand, CXRF can

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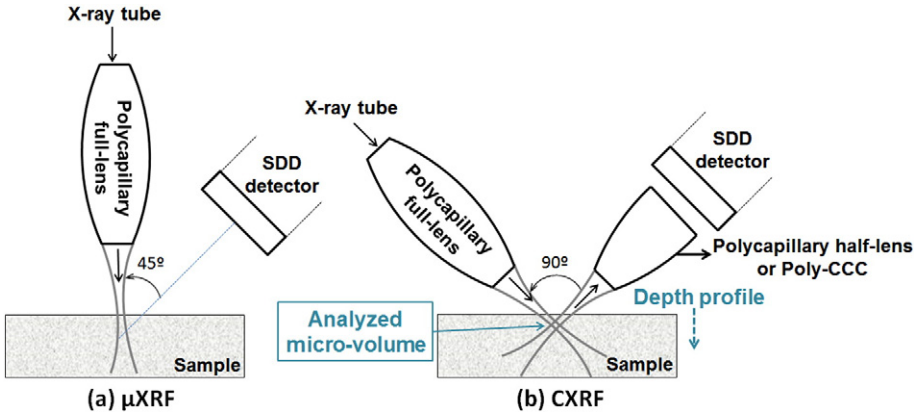

Fig. 1. (a) Configuration of μXRF and (b) CXRF technique.

provide depth-resolved information (3D analysis), but other X-ray emission-based techniques can do it as well as

- classic XRF and μXRF [14–19],
- PIXE and RBS [17],
- μPIXE [20,21].

On the other hand, in the study of artworks, CXRF is mostly used to obtain depth profiles (1D study) or 2D profiles [8,22,23]. The 3D study of paintings can be very time-consuming and does not provide additional information respect to 2D analysis. In 2005, Kanngießer et al. [24] published the first CXRF study of experimental paint layers. In 2009, the first CXRF depth analysis applied in Cultural Heritage of Japanese lacquerware 'Tamamushi-nuri' was published by Nakano and Tsuji [13]. In 2012, the first CXRF study of Renaissance paintings was published by Reiche et al. [12]. In this study, the CXRF depth profiles obtained on the paintings were related to lateral CXRF scans on cross sections. The cross sections were prepared from samples taken next to the analyzed points in order to better evaluate the performance of CXRF depth profiling for the analyses of paint layers. The cross sections were also studied by optical microscope (OM) and SEM-EDX in order to compare the results to those obtained by CXRF [12].

Indeed, this strategy was chosen knowing that the main X-ray interfering effect which limits CXRF is the absorption effect. It occurs when either primary or secondary X-rays are absorbed within the sample. When X-ray passes through a sample of thickness D, the primary intensity I_0 is reduced to I according to the Lambert–Beer law:

$$I = I_0 e^{-\mu_{lin} D} = I_0 e^{-\mu \rho D} \quad (1)$$

where μ_{lin} is the linear absorption coefficient, μ is the mass absorption coefficient and ρ is the density of the medium.

The mass absorption coefficient depends on energy but also on the chemical element. This coefficient for a multi-element attenuator μ_{total} can be expressed as a weighted average:

$$\mu_{total} = \sum_{i=1}^{n} W_i \mu_i \quad (2)$$

where W_i and μ_i, respectively, are weight fraction and mass absorption coefficient for element i.

As can be seen, the absorption effect limits the maximum probing depth from which the signal can be registered. For any given element, the attenuation length can be defined as a probing depth from which the registered intensity drops to 36.7% of the maximum value [25]. The attenuation length depends on the overall composition of the sample. It decreases for samples with a higher atomic number and density and increases with the energy of X-ray emitted.

This phenomena can drastically affect the CXRF multilayered paintings results. The Gaussian shape of the depth profile and the information obtained from this Gaussian are modified.

Fig. 2. General view of the μXRF-CONCHA setup doing *in situ* analysis of "San Pedro Nolasco despidiéndose de Jaime I El Conquistador."