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Editorial

Contribution of X-ray Fluorescence Techniques in Cultural Heritage Materials Characterization

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1. Introduction

Archaeometry and cultural heritage have lately taken great advantage of developments in scientific techniques, offering valuable information to archaeology, art history, and conservation science, involving both instrumental and non-instrumental approaches. Among the possible techniques, X-ray Fluorescence (XRF) has become one of the most applied techniques for cultural heritage elemental material characterization, due to its user-friendliness; fast, short acquisition times; portability; and most of all, its absolutely non-destructive nature. For this reason, besides often being a first choice for a preliminary overall materials investigation, XRF spectrometers and spectra data handling methods have continuously improved, giving rise to many variations of the same technique; portable spectrometers, micro-probes, and large area scanners are all variations of a very flexible technique.

2. Review of Issue Contents

This Special Issue collects papers dealing with several analytical techniques and applications related to XRF spectroscopy, with special attention toward the application to cultural heritage materials. Paper subjects include instrumentation and technical developments, case studies on various materials requiring methodological innovations, and new data handling. Beside traditional XRF configuration, both energy dispersive and wave dispersive, Macro-XRF and the use of synchrotron radiation have also been considered. Indeed, most of the variations of XRF spectroscopy have been considered: portable or mapping spectrometers, synchrotron based XRF, and synergic association with other non-destructive analytical techniques.

In the paper by Ruschioni and co-authors [1], the project for a low-cost home-made XRF portable spectrometer is presented, for all those cases where there is not enough financial support to buy a commercial device. The FUXYA2020 spectrometer was intended mostly for cultural heritage (CH) applications and meets the requirements for both low Z matrix objects, such as glasses and ceramics, and medium-high Z materials, such as metals. First application shown (on pigments, ceramics and gold alloys) demonstrate that a simple and inexpensive prototype can be of great help for a rapid and reliable characterization of cultural heritage materials whenever commercial devices are unaffordable.

Portable instrumentation was also used in [2,3]. In the former paper, a mandolin by Antonio Stradivari has been investigated for the first time by non-invasive reflection Fourier transformed infrared (FT-IR) spectroscopy and X-ray fluorescence (XRF) on different areas previously selected by UV-induced fluorescence imaging. The combined spectroscopic approach allowed us to hypothesize original materials and finishing procedures similar to those used in violin making, and XRF results proved to be essential to support FT-IR findings and to detect possible iron-based pigments in the finishing layers. The paper by Fornacelli et al [3] presents a provenance study on ceramic sherds by means of portable XRF instrumentation coupled with statistical analysis. Indeed, the combined application

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of this kind of analytical technique and statistical analysis to the investigation of a large repertory of ceramic fragments allowed for the grouping of the assemblage by identifying geochemical clusters. Assuming a correlation between compositional patterns and local production centers, cultural relations between communities and regions were investigated starting from the pottery manufacturing and trade.

WD-XRF (wave dispersive XRF) was instead exploited in the work by Fragata and co-authors [4], where the floor mortar layers of the high imperial mosaics of a Roman housing in Braga, Portugal, were investigated, showing that their composition was clearly related to the stratigraphic position and to the external conditions and treatments to which they were submitted.

A few papers were devoted to macro-XRF (MA-XRF) instrumentation and related issues. The traditional field of application in CH materials, i.e., painting, was the subject of a research in the frame of the INFN-CHNet, the Cultural Heritage Network of the Italian National Institute of Nuclear Physics. They designed and developed an MA-XRF scanner easy to transport for in situ use. In the paper submitted for this special issue [5], they present results of a painting by the Flemish artist Rogier van der Weyden, belonging to the collection of the Uffizi gallery in Florence, Italy. The painting was analyzed during conservation treatments at the Opificio delle Pietre Dure in Florence. Also in this case, MA-XRF proved to be a powerful technique that can be easily utilized as an early non-invasive and non-destructive analytical method as a guide for a subsequent, more accurate, scientific analysis. The same scanner was used in the work by Sottili et al. [6] for an uncommon application to furniture at the Centro di Conservazione e Restauro "La Venaria Reale" (Turin, Italy), a leading conservation center in the field. The use of the MA-XRF technique on furniture has provided information on the elemental–spatial distribution of the decorative layers, such as gilding and ivory, on the polychromatic surfaces of a chinoiserie lacquered cabinet of the 18th century and a desk by Pietro Piffetti (1701–1777).

Again on MA-XRF, the work by Orsilli and co-authors [7] summarizes the advantages and limitations of MA-XRF, here considered as an imaging technique. This allows a better synergy with other hyperspectral methods, or the combination with spot investigations. A pioneering analysis protocol (STEAM) based on the spectral angle mapper algorithm is also presented, unifying the MA-XRF standard approach with punctual XRF, exploiting information from the mapped area as a database to extend the comprehension to data outside the scanned region, and working independently from the acquisition set-up.

Last, but of great interest, is a paper regarding synchrotron X-ray μ- and nano-probes applied to CH materials, in particular to ancient ceramics study [8]. Fine and varnished wares are the case study for exploring challenges offered by synchrotron X-ray microprobes optimized to collect microchemical and phase-distribution maps, capable of providing relevant clues for discriminating workshops and exploring technological aspects, which are fundamental in answering the current archaeological questions on ceramic findings.

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References

1. Ruschioni, G.; Micheletti, F.; Bonizzoni, L.; Orsilli, J.; Galli, A. FUXYA2020: A Low-Cost Homemade Portable EDXRF Spectrometer for Cultural Heritage Applications. *Appl. Sci.* **2022**, *12*, 1006. [CrossRef]
2. Volpi, F.; Fiocco, G.; Rovetta, T.; Invernizzi, C.; Albano, M.; Licchelli, M.; Malagodi, M. New Insights on the Stradivari Coristo Mandolin: A Combined Non-Invasive Spectroscopic Approach. *Appl. Sci.* **2021**, *11*, 11626. [CrossRef]
3. Fornacelli, C.; Volpi, V.; Ponta, E.; Russo, L.; Briano, A.; Donati, A.; Giamello, M.; Bianchi, G. Grouping Ceramic Variability with pXRF for Pottery Trade and Trends in Early Medieval Southern Tuscany. Preliminary Results from the Vetricella Case Study (Grosseto, Italy). *Appl. Sci.* **2021**, *11*, 11859. [CrossRef]
4. Fragata, A.; Ribeiro, J.; Candeias, C.; Velosa, A.; Rocha, F. Archaeological and Chemical Investigation on the High Imperial Mosaic Floor Mortars of the Domus Integrated in the Museum of Archaeology D. Diogo de Sousa, Braga, Portugal. *Appl. Sci.* **2021**, *11*, 8267. [CrossRef]
5. Mazzinghi, A.; Ruberto, C.; Castelli, L.; Czelusniak, C.; Giuntini, L.; Mandò, P.; Taccetti, F. MA-XRF for the Characterisation of the Painting Materials and Technique of the Entombment of Christ by Rogier van der Weyden. *Appl. Sci.* **2021**, *11*, 6151. [CrossRef]
6. Sottili, L.; Guidorzi, L.; Mazzinghi, A.; Ruberto, C.; Castelli, L.; Czelusniak, C.; Giuntini, L.; Massi, M.; Taccetti, F.; Nervo, M.; et al. The Importance of Being Versatile: INFN-CHNet MA-XRF Scanner on Furniture at the CCR "La Venaria Reale". *Appl. Sci.* **2021**, *11*, 1197. [CrossRef]
7. Orsilli, J.; Galli, A.; Bonizzoni, L.; Caccia, M. More than XRF Mapping: STEAM (Statistically Tailored Elemental Angle Mapper) a Pioneering Analysis Protocol for Pigment Studies. *Appl. Sci.* **2021**, *11*, 1446. [CrossRef]
8. Gianoncelli, A.; Kourousias, G.; Schöder, S.; Santostefano, A.; L'Héronde, M.; Barone, G.; Mazzoleni, P.; Raneri, S. Synchrotron X-ray Microprobes: An Application on Ancient Ceramics. *Appl. Sci.* **2021**, *11*, 8052. [CrossRef]