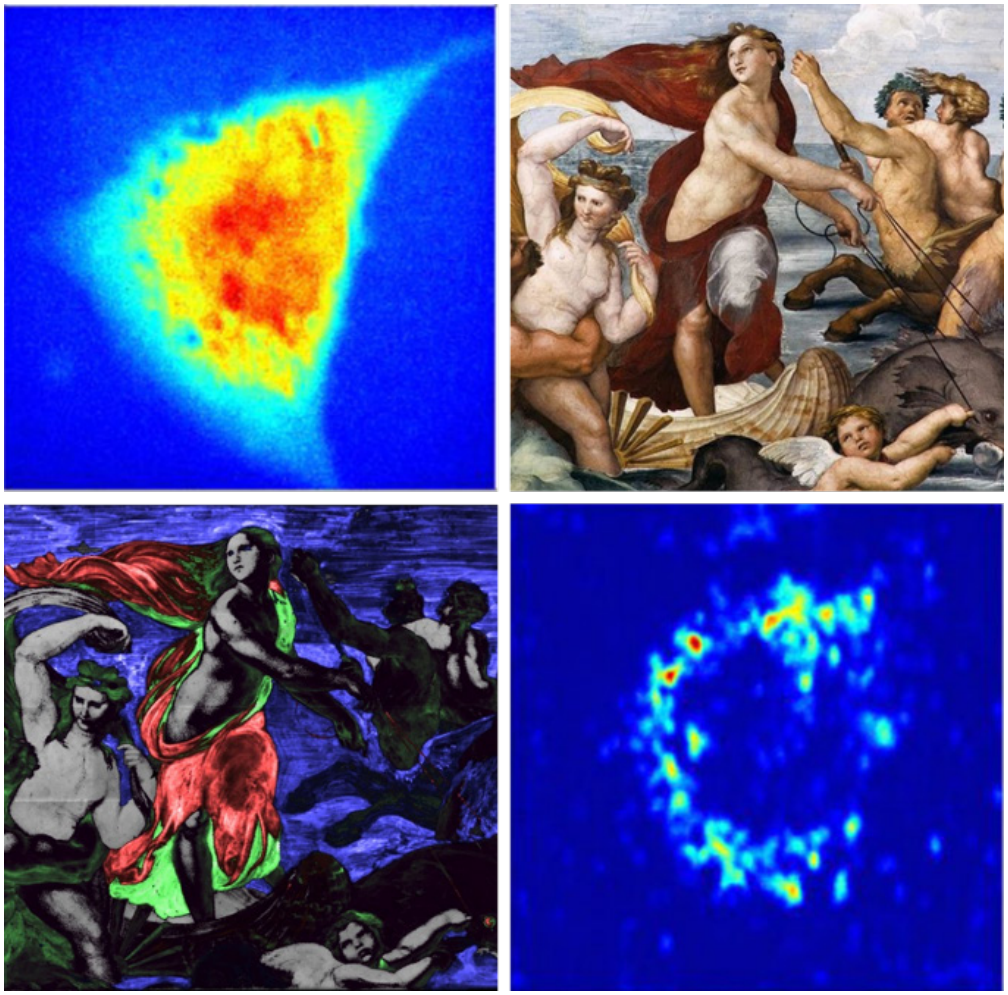
APPLICATION Note # 1

DANTE: Fast X-ray Fluorescence Mapping



Abstract

X-ray Fluorescence (XRF) is an analytical technique widely adopted in different applications such as biology, medicine research, earth science, art conservation and restoration and many others. XRF mapping is becoming an important technique to reveal elemental distribution over a given area of the sample of analysis. From pigment distribution in large paintings and frescos to nanoparticles displacement in biological cells, X-ray mapping is becoming a fundamental tool to reveal ancient artists secrets or to discover new ways to treat diseases. In this document, we'd like to introduce some of the unique features of the DANTE Digital Pulse Processor for XRF mapping.

Images of the Triumph of Galatea by Raffaello Sanzio Courtesy of Villa Farnesina, Rome, Italy.
Images of an X-ray Map of a fibroblast cell exposed to CoFe2O4 nanoparticles is Courtesy of TwinMic beamline Elettra-Sincrotrone, Trieste, Italy.

Introduction to XRF

X-ray fluorescence (XRF) is a technique which allows the measurement of atomic species constituting a sample under analysis. This technique is widely adopted for elemental or chemical analysis.

Figure 1. Schematic representation of the fluorescence effect(a) Ejection of a K-shell electron (b) L-shell electrons filling the K-shell vacancy and releasing a fluorescence photon

If a photon with sufficient energy hits an atom, it may cause an electron from inner shells to be ejected from the atom. An electron from an outer shell may fill up the vacancy of the inner shell releasing some energy in the form of an X-ray photon proportional to the energy difference between the two shells.

The energy of this radiation is a unique signature of the atom emitting it. This phenomenon is called X-ray fluorescence (XRF). In **Figure 1a**, the example of the ejection of an electron of the K-shell is represented. The vacancy is then filled up by an electron from the L-shell, see **Figure 1b**, which causes the emission of the so called Kα X-ray photon. Transitions from M to K shells or from M to L are called Kβ and Lα respectively. By measuring the energies of these photon emissions, it is possible to precisely identify which atomic species are composing the sample under analysis.

A modern XRF setup, see **Figure 2** consits of an X-ray source (X-ray tube or synchrotron light beam), used to excite the sample under analysis on a certain spot, a sensor capable of detecting the photons generated by the fluorescence effect and by a digital pulse processor (DPP). The DPP is responsible for digitizing the sensor signal, for filtering each photon pulse computing its energy value and ultimately building the so-called energy spectrum by creating an histogram of the photon energies detected.

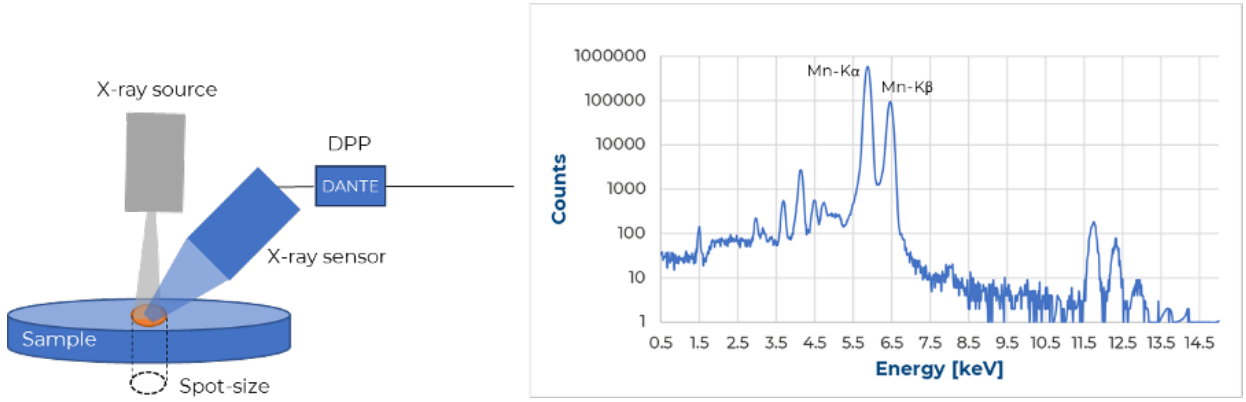


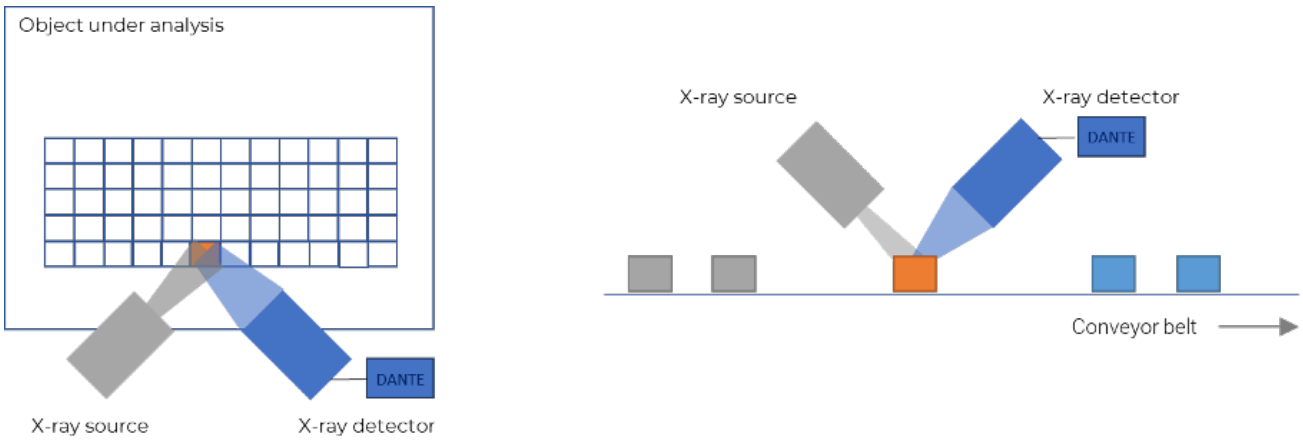
Figure 2. Modern XRF setup: an X-ray source excite the sample under analysis on a certain spot, an X-ray sensor collects the fluorescence photons and a Digital Pulse Processor computes the final energy spectrum by counting the number of photons belonging to each energy bin (often called "channels"). A dedicated analysis software can then be used to associate each peak in the energy spectrum to the corresponding atomic species.

XRF Mapping or Scanning

X-ray Fluorescence (XRF) mapping or scanning are well-established techniques used in a wide range of scientific applications.

In the case of mapping, the sample under analysis is kept still while the X-ray excitation source moves across a certain area of analysis, see **Figure 3a**; the X-ray detector can either move together with the excitation source or stay still in one position. The XRF emission signal is acquired for each position, resulting, after suitable analysis, into a set of elemental maps.

In other applications, such as in-line monitoring systems, the samples move under the XRF detection system on a conveyor belt and their elemental composition is scanned by the collection of sequential points of measurement, see **Figure 3b**.



(a) (b)

Figure 3. X-Ray Fluorescence used for different applications: XRF mapping of large objects (a), in-line XRF scanning of objects moving on a conveyor belt (b).

In either cases of XRF mapping or in-line scanning, both the energy resolution of the detector and the time required to compute a single energy spectrum are of paramount importance.

In X-ray mapping, these parameters determine the total time required to perform a map with a certain quality, while in in-line scanning they limit the number of points that can be acquired for each sample moving on the conveyor belt. The digital pulse processor plays a fundamental role in defining these two parameters.

DANTE Mapping mode

The DANTE digital pulse processor was built and designed to allow fast XRF mapping and/or scanning while maximizing energy resolution.

DANTE offers indeed the unique feature to acquire multiple spectra down to 1 ms/spectrum without dead-time between consecutive spectra allowing very fast consecutive pixel acquisitions in maps or multiple line points in scanning applications, see **Figure 4a**. Of course, when such short acquisition times are used, it is also required that enough photons are detected to compute a useful energy spectrum.

The number of fluorescence photons generated per second are determined by the X-ray source flux and by the DPP filtering capabilities. DANTE allows the user to select different peaking times values down to 32 ns ensuring outstanding Output Count Rate (OCR) vs. Input Count Rate (ICR) performances with state-of-the-art energy resolution performance, see **Figure 4b**, **c**.

The ICR corresponds the number of XRF photon arriving onto the detector, while the OCR to the number of photons effectively detected and correctly processed by the electronics.

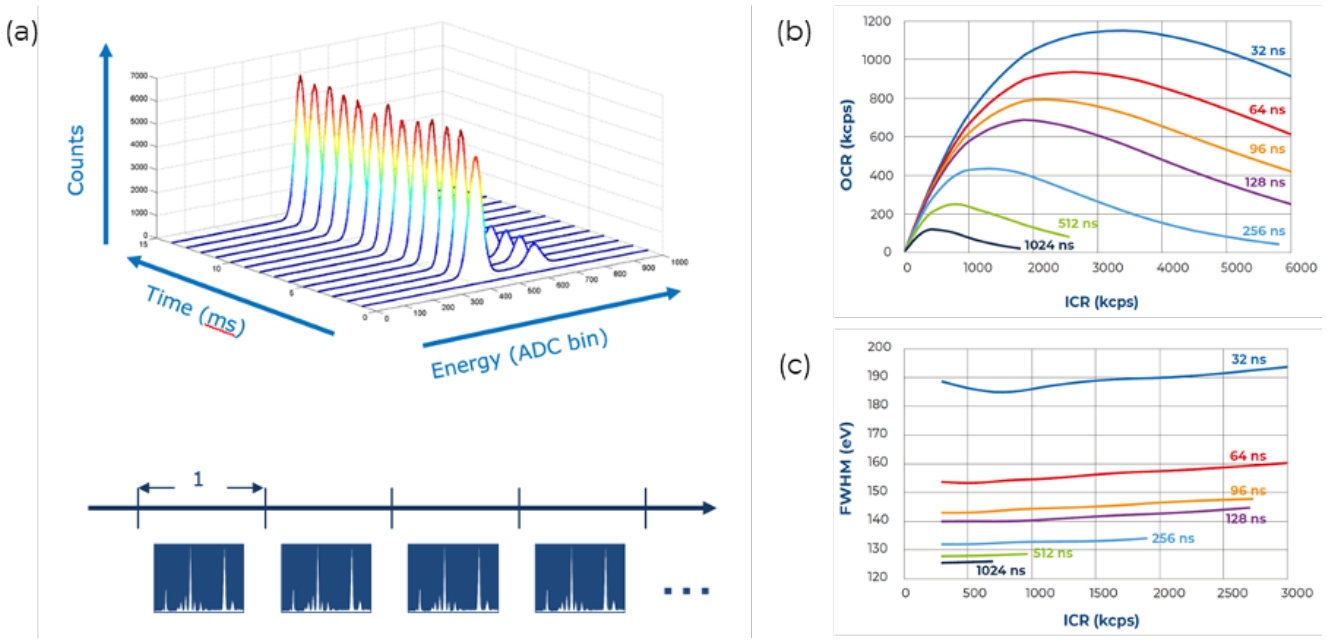


Figure 4. (a) DANTE mapping mode capabilities of acquiring spectra with zero-dead-time between spectra. (b) ICR vs. OCR plot at different peaking times with DANTE coupled to a Silicon Drift Detector(c) Energy resolution or FWHM @Mn Kα at different peaking times.

DANTE is designed such that it can accept as input an external digital signal to be used to control the generation of the output spectra data. In mapping systems this feature is used to synchronize the spectra acquisition with the movement of the x-ray source over the area of analysis, namely the "pixel", thus with the corresponding pixel enabling the elemental map reconstruction. The external logic input can be used as Gate or Trigger signal.

In Gated mode, a new spectrum is acquired every time the gating input is either low or high, while in triggered mode the DPP is always active, and a new spectrum is initialized every time an edge on the input trigger signal occurs. See **Figure 5**, for the different gate/trigger mode supported by DANTE.

The mapping mode is available to the user through the DANTE acquisition software or through a dedicated API which can be used to easily integrate DANTE functionalities into the user control software.

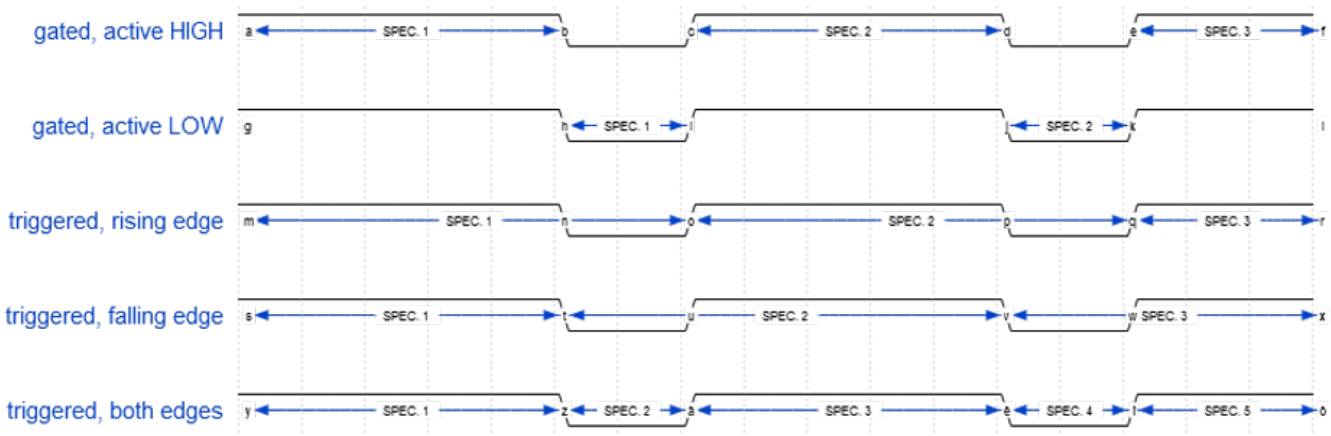


Figure 5. Gating and Trigger modes supported by the DANTE DPP in Mapping mode

XRF Mapping of Fibroblast Cells at ELETTRA

DANTE DPP was used at the TwinMic soft X-ray microscopy synchrotron beamline [1] (Elettra–Sincrotrone Trieste, Trieste, Italy) to image the elemental concentration over some fibroblast cells exposed to $CoFe_2O_4$ nanoparticles.

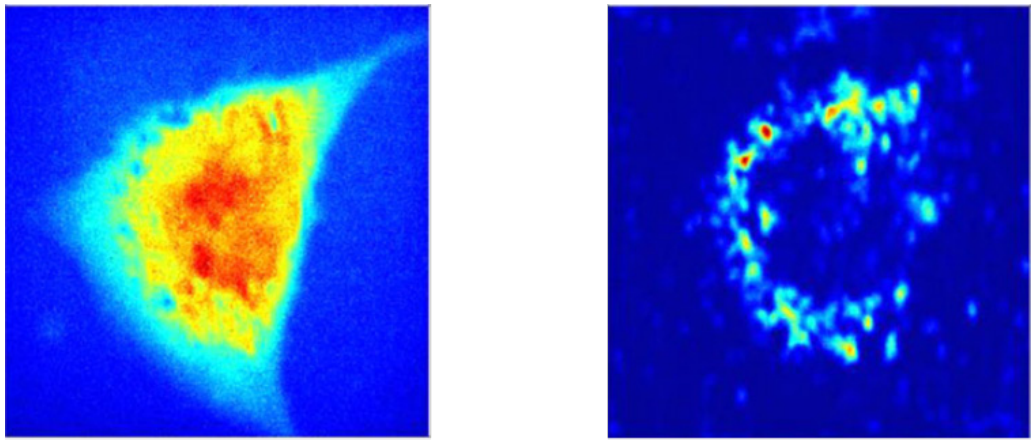


Figure 6. Elemental mapping obtained on a fibroblast cell exposed to $CoFe_2O_4$ nanoparticles obtained at TwinMic synchrotron beamline with DANTE 8CH. (a) Compton and Rayleigh scattering image (b) Fe and Co elemental distribution.

Different elemental maps of an area of 50 × 50 µm over a single cell were obtained with DANTE 8CH and the 8 SDD detectors working under vacuum condition at TwinMic. **Figure 6** reports the maps obtained by setting the spot size to about 850 nm, the excitation energy at 1.08 keV and the pixel size (movement step of the excitation spot across the cell) of the map to 187 nm, producing a 269 × 269 pixels image. The dwell time per pixel was fixed to 0.6 s, resulting in a total acquisition time per map of about 13 hours. In figure 4, the energy spectrum sum is reported for the whole XRF acquisition, showing outstanding performance of DANTE in combination with the TwinMic beamline setup at low energies by the identification of C, N, O, Fe and Co peaks.

In XRF mapping, the generation of the spectra from DANTE is synchronized with the motors used to move the focus of the synchrotron beam pixel by pixel. These motors are often driven by or generate a SYNCH signal which can be used as gating or trigger input for DANTE used in Mapping mode as described in previous section.

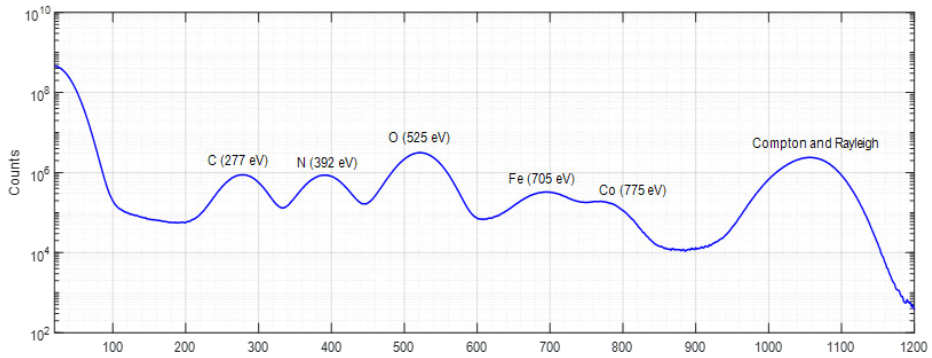


Figure 7. Energy spectrum of the complete acquisition on the fibroblast cell exposed to $CoFe_2O_4$

XRF Mapping of Large Paintings and Frescos

The Digital Pulse Processor plays a relevant role also in large paintings or frescos. Here, one of the main aims of X-ray mapping is to correctly identify the pigments used by ancient artist to study their technique or even more important to correctly perform restoration campaign. Famous artworks are not always available to scientists as they are often exposed in art exhibitions. The time reserved to the analysis is always of big concern. Let us consider a simple example of the x-ray mapping of a painting of 1 m x 1 m dimensions to be scanned with 1 mm pixel size. The complete map would result in a 1 Megapixel image.

As said, in XRF mapping the pixel is defined by the excitation source which scans the artworks pixel by pixel, therefore the total acquisition time is calculated as the acquisition time per pixel (or per spectra) multiplied by the number of pixels to be scanned. Considering a time of acquisition of 40 ms/pixel a total time of about 11 hours would be required to complete the XRF scan, assuming no dead time is introduced by the electronics performing the XRF measurement.

DANTE mapping functionality is optimized exactly to minimize the time per spectrum and to ensure zero-dead time between consecutive pixels, allowing the so called on-the-fly XRF mapping. In this acquisition mode, the X-ray source and the detection system are continuously moving across the artwork by a system of motorized frames or slits. The digital pulse processor must continuously acquire spectra and at the same time it synchronize with the motors to correctly associate the pixel acquisition to the motor position.

In **Figure 8a** and **b**, the optical image and the XRF maps of the “Trionfo di Galatea” by Raffaello Sanzio are reported. These images are the result of a collaboration between ENEA, IRET-CNR, Laboratorio di Diagnostica per i Beni Culturali di Spoleto and XGLab – Bruker Nano Analytics [2]. The “Trionfo di Galatea” is a huge (295 cm x 225 cm) fresco conserved at Villa Farnesina in Rome and the DANTE functionalities were fundamental to shorten the measurement time required to perform the XRF maps.

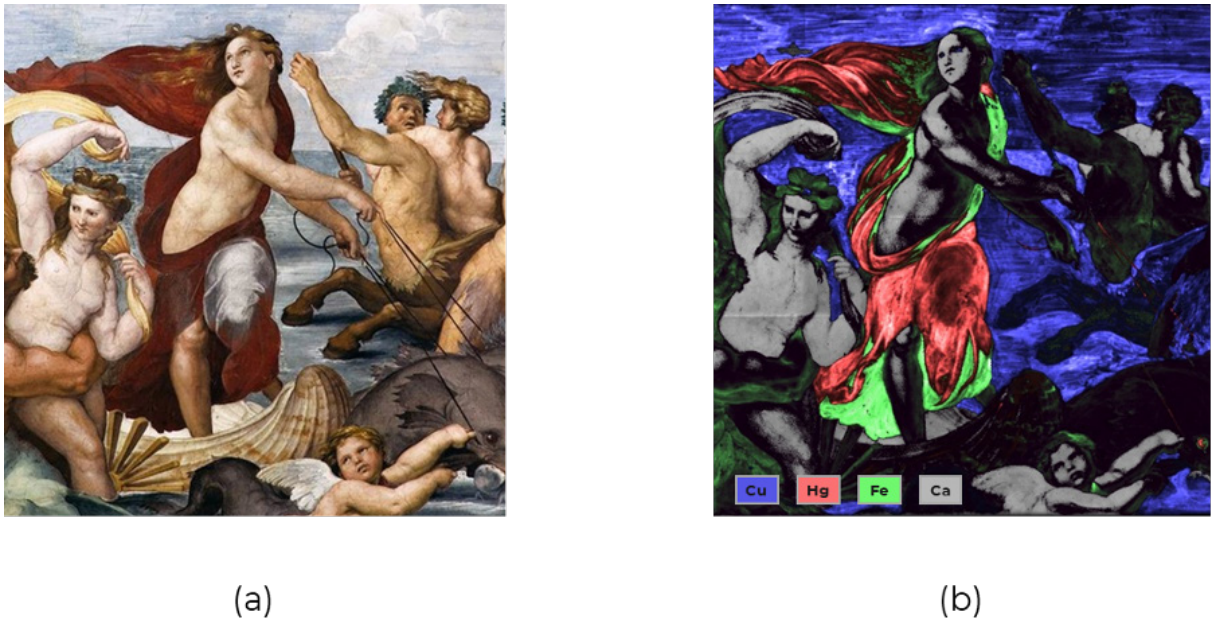


Figure 8. X-ray fluorescence map on the "Trionfo di Galatea" by Raffaello Sanzio. (a) optical image (b) XRF map highlighting distribution of different elements: Cu (blue), Hg (red), Fe (green), Ca (grey)

Bibliography

[1] L. Bombelli, M. Manotti, M. Altissimo, G. Kourousias, R. Alberti and A. Gianoncelli, "Towards on-the-fly X-ray fluorescence mapping in the soft X-ray regime," X-Ray Spectrometry, vol. 48, no. 5, pp. 325-329, 2019.

[2] C. Anselmi, M. Vagnini, C. Seccaroni, M. Azzarellli, T. Frizzi, R. Alberti, M. Falcioni and A. Sgamellotti, "Imaging the antique: unexpected Egyptian blue in Raphael's Galatea by non-invasive mapping," Rend. Fis. Acc. Lincei, vol. 31, no. December, p. 913–917, 2020.