



From Raphael (La Deposizione) to Raphael (La Fornarina): a Circumnavigation Accompanying the Evolution of Energy-Dispersive XRF Devices

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Abstract

This paper describes history and technical evolution of portable devices which use energy-dispersive X-ray fluorescence (EDXRF)-analysis to study works of art. The history starts in 1971, when the first transportable equipment was employed to examine the pigments of Raphael's painting "La Deposizione" during restoration at the "Istituto Centrale del Restauro" in Rome. Then, paintings of all types were analyzed and metals (bronzes, brasses, gold and silver). The evolution of the exciting source is described (from radioisotopes or big size X-ray tubes, to miniaturized, dedicated X-ray tubes) and of X-ray detectors (from proportional gas counters, to N₂-cooled Si or Ge-detectors, to Peltier cooled HgI₂ and Si-PIN, to Peltier cooled Si-drift). Also, the pulse height analyzers had an important evolution, from a heavy box to a computer card, to very small electronic circuits included in the detector box. The most "modern" portable EDXRF device is currently composed of a small-size X-ray tube, a Si-drift detector, both properly collimated, a portable computer, and dedicated software for the processing of the data. The total weight of such a device is about 2 kg. The last evolution: from analysis of a limited number of points to a complete scanning of the artifact. A mechanics is also required, with a sophisticated software interfacing mechanics to measuring heads. Maps giving the distribution of all analyzed elements in all areas of the painting "La Fornarina" by Raphael could be obtained. Finally, an accurate analysis of the K or L-X rays of the elements present in the paintings allowed to determine the disposition of the pigment in the correct layer.

Keywords XRF · Radioisotopic sources · X ray tube · Cryogenic detectors · SDD detector · MA XRF

This paper is dedicated to our friend and mentor professor Sergio Mascarenhas. Sergio was not only an excellent physicist, but he was also a great lover of the arts, and particularly of the Italian Renaissance. He particularly adored Raphael and everywhere Sergio was active, there was a copy of "the school of Athens," a well-known masterpiece by Raphael. Sergio was also curious about the correlation between Science and Art, and was always anxious about the progress of scientific methods applied to studies of artifacts. For this reason, we organized in Alghero, Italy, a symposium in his honor, for his 70 years, and now, we dedicate to him this paper, which concerns analyses with X-rays of Raphael's paintings. Sergio was not only a great scientist and a great Brazilian. He was also a great friend, liked jokes, and was full of joy of living and sense of humor, as shown in Fig. 17 photo, taken at the Institute for Advanced Studies of Princeton, where he was invited in 1996.

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1 Introduction and Evolution of EDXRF-Devises

The use of energy-dispersive X-ray fluorescence (EDXRF)-analysis to determine pigments in paintings and metals, to our knowledge, starts in 1971, and the first paper "Non-destructive analysis of chemical elements in paintings and enamels" by R. Cesareo et al., from the Institute of Physics, Faculty of Engineering, University of Rome, and M. Marabelli et al., from the Central Restoration Institute, Rome, was published in 1972 [1]. The paper was published in Archaeometry and reported EDXRF-analysis of various paintings, among them the "Deposition" by Raphael, located at Galleria Borghese (Fig. 1), Rome. The paintings

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Fig. 1 The “Deposition” by Raphael painted in 1507. It is exposed in the Galleria Borghese in Rome



Fig. 2 Equipment employed to analyze the “Deposition” by Raphael and other paintings at the Central Restoration Institute of Rome. It is analyzing the “Madonna con bambino” by Lucas Cranach. Main Parts: (2): measuring head with radioisotopic source and gas proportional counter; (3) measuring head with radioisotopic source and NaI(Tl)-detector (not employed); (4) electronic chain; (5) LABEN multi-channel analyzer

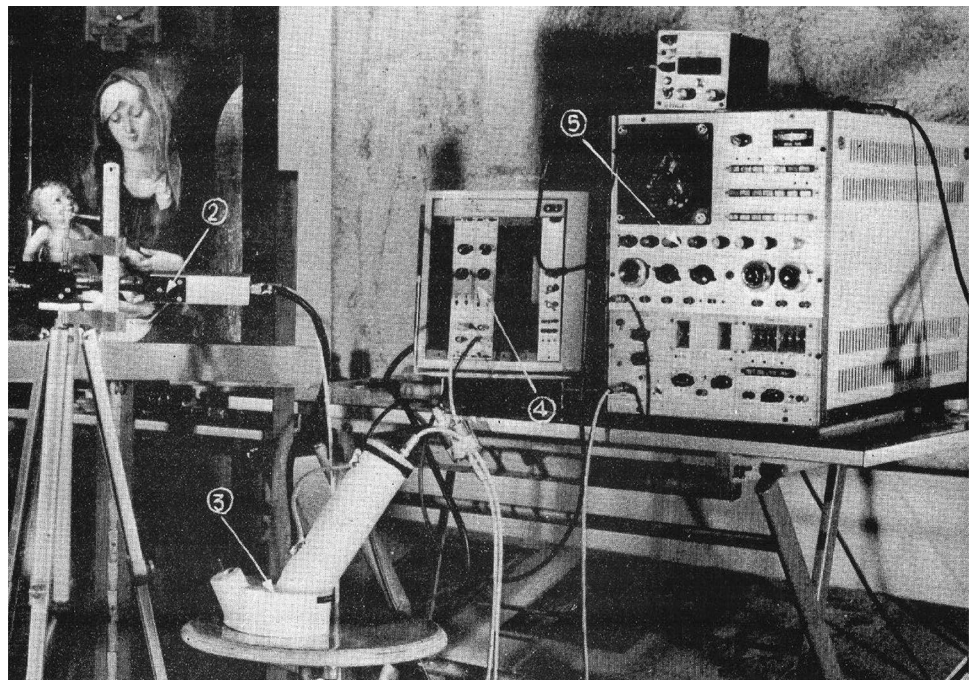
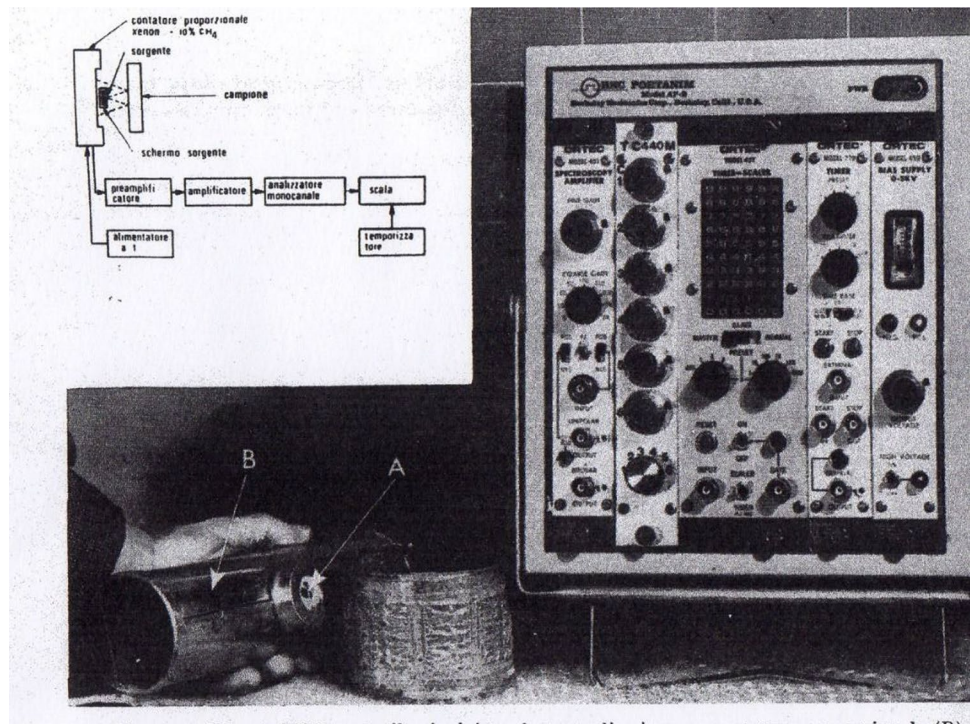


Fig. 3 Portable device for analysis of metals (1972). From left: proportional gas counter (B) with radioactive source in the middle of the Be-window (A); electronics for the detector. Home-modified S.C.A. (TC440M) with six windows prefixed on intervals of energy corresponding to the elements to be analyzed, and a switch (on the bottom). The S.C.A. is followed by a timer-scaler. An Etruscan bracelet from the Tomb Regolini-Galassi (Vatican Museum) is being analyzed



were analyzed at the Istituto Centrale del Restauro, Rome, where they were under restoration.

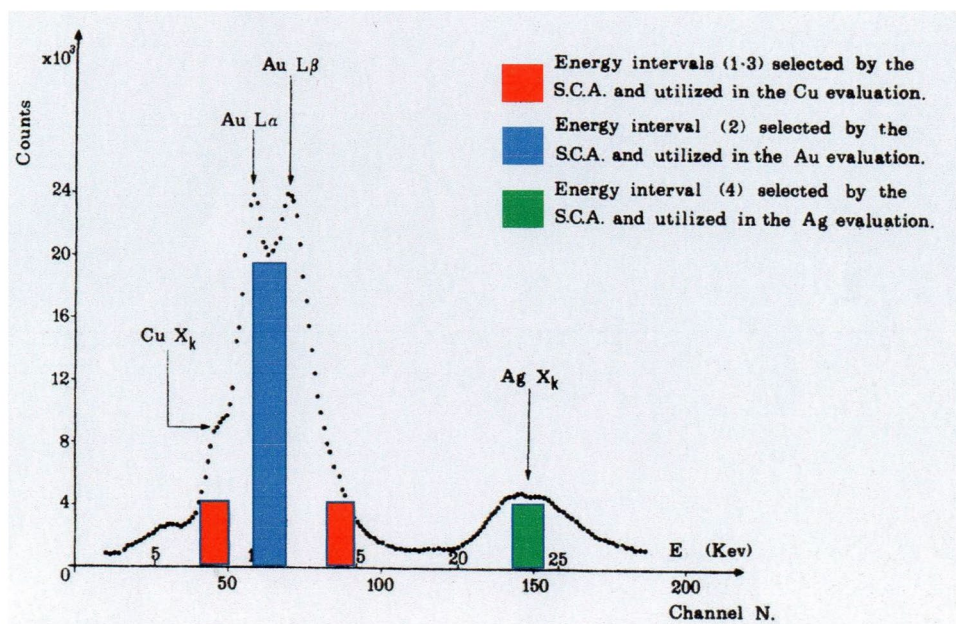
The equipment used at the time, 48 years ago, may be considered today rather primitive, being composed of a radioactive source (of Cd-109, Am-241, Pm-147 or Co-57), or Kr, Ne, or Xe gas proportional counters with an energy resolution of about 18% at the energy of 6.4 keV (iron $K\alpha$ -line) [2] and an electronic chain coupling the detector to a LABEN 400 pulse-height analyzer. The device had a

total weight of about 50 kg and was transportable, not portable (Fig. 2).

Due to the poor energy resolution, the X-ray spectra were not easy to process. However, it was possible to get the following:

- identify the typical pigments used by Raphael: malachite, lead-tin yellow, white lead, lapis lazuli, a Cu-pigment, cinnabar, azurite, ochre.

Fig. 4 EDXRF spectrum of a Au-alloy (Au=75%, Ag=18%, Cu=7%) measured with a proportional gas counter and registered with a MCA. The energy intervals are also shown, which were used to determine Au, Ag, and Cu concentration with a S.C.A. in which the fixed window can be switched in four possible positions: Cu-counts (red); difference red-left minus red light; Au-counts (blue); Ag-counts (green). The Cu concentration, given by the difference between left and right red rectangles, must be 0. The very poor energy resolution is apparent and may be compared, for example, with the gold XRF spectrum shown in Fig. 10



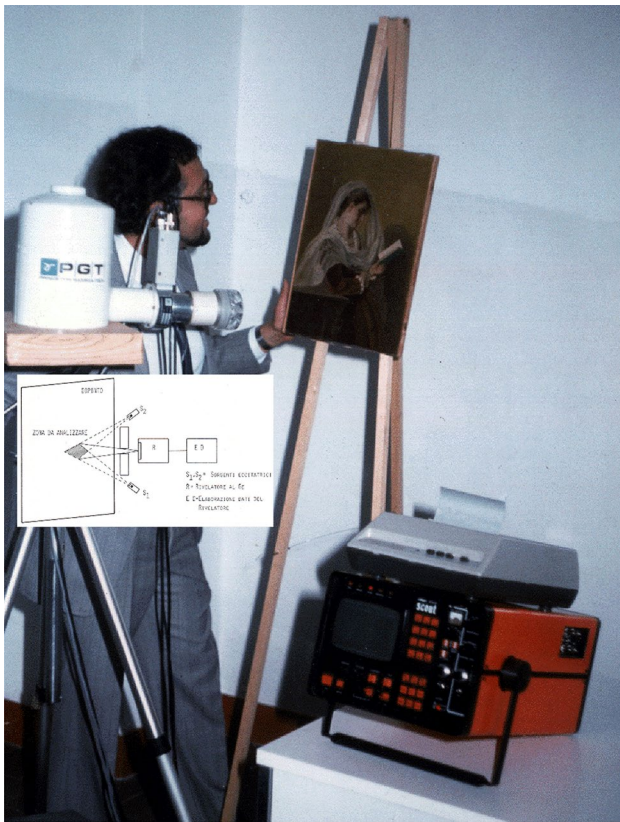


Fig. 5 Image of the device that used Am-241 (emitting 59.6 keV gamma rays) sources in confocal configuration used at the beginning of the eighties in various campaigns of measurements in Italian museums [10]

- identify areas of modern restoration, through identification of “modern pigments” based on the detection of Zn-white and Ti-white industrially produced around 1850 and 1920 respectively [3], but also by pigments based on chromium, selenium, and cadmium produced only recently. The last point was particularly important for the restoration of the painting, and the restorers removed the pigment layer containing “modern” pigments.

Approximately at the same time, a portable EDXRF equipment was developed and used to analyze ancient metals (bronzes, brasses, gold, silver....) in museums, churches, open air, and so on. This equipment was characterized by a radioactive source, a gas proportional counter, and a single-channel analyzer (SCA) coupled to a scaler. The SCA was modified in order to select, keeping fixed the window (interval of energy). Six switchable channels determine the energy of well-defined single elements (for example, in the case of bronzes Cu, Sn, Pb; in the case of gold Au, Ag, and Cu). In such a manner, a portable equipment was constructed, able to analyze only selected elements, but with poor sensitivity. The device is shown in Fig. 3, and a typical gold EDXRF-spectrum showing how the SCA works is shown in Fig. 4 [4–6].

With such a device, Etruscan, Roman, and Greek bronzes were analyzed [4, 5], as well as Etruscan gold objects from various tombs and in museums, such as the pectoral (~675–650 B.C.) from the tomb Regolini-Galassi exposed at the Vatican Museum [6].

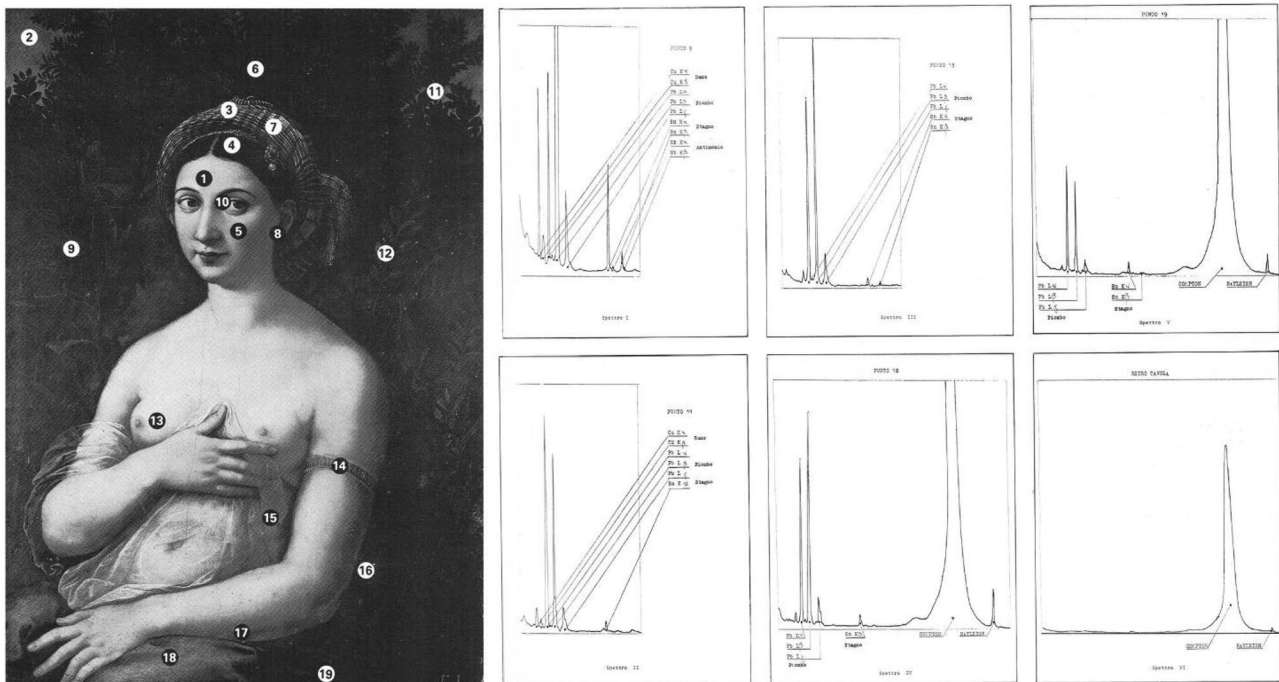


Fig. 6 Measurement points and some results of the study of 1983 on Raphael table “La Fornarina,” using the device of the Fig. 7. It is possible to note the characteristic shape of the spectrum which presents at high energies the scatter peaks on the table by penetrating 60 keV photons [7]

Fig. 9 EDXRF device for elemental analysis of frescos in the Chapel of the Scrovegni, painted by Giotto in Padua between 1303 and 1305. Two measuring heads were employed: one composed of a Hamamatsu X-ray tube working at 10 kV and 1 mA, and a Si-PIN detector, for the analysis of sulfur; the second composed of an Oxford X-ray tube with Mo-anode, for analysis of medium-high Z elements, is composed of a mini X-ray tube working at 30 kV and 500 μ A and a Si-PIN detector



in situ. However, the HgI_2 detector revealed itself to be delicate versus time, and the Si-PIN was, therefore, generally preferred for portable devices, despite an important negative point: they accept only a reduced number of photons per second without losing energy resolution greatly increasing the required measuring time. Paintings and, for the first time, frescos were analyzed with the Si-PIN detector. Frescos from the church of S. Stefano Rotondo in Rome, painted by Antonio Tempesta in the year 1568, from the “Nolfi chapel” in the cathedral of Fano painted by Domenichino in 1618–1619 [14], from the church of S. Francesco in Arezzo painted by Piero della Francesca in 1452–1466 and from Giotto’s frescos in the chapel of the Scrovegni, painted in Padua in 1303–1305 (Fig. 9) [15, 16]. In frescos, the background is composed by plaster (CaCO_3)

that becomes CaSO_4 and/or Cl (NaCl), due to pollution close to the sea. Then, alloys were analyzed such as the four panels from the Volvinius altar in the Basilica of St. Ambrose in Milan (824–859 A.C.) on gold and gilded-silver [17], the big sphere on gilded bronze located at the top of the basilica of St. Peter in Rome, and the famous marble statue of David by Michelangelo, particularly to detect and remove S due to pollution [18].

The described devices allowed to analyze circular areas of the order of 0.1 mm^2 corresponding to circles with diameter of about 0.5 mm. To analyze much smaller areas, the method of capillary collimators developed by Kumakhov at the end of eighties [19] was also applied to a few cases, such as the analysis of a very small gold fragment from the God’s halo in the Chapel of the Scrovegni (Fig. 10).

Fig. 10 EDXRF spectrum of a very small fragment of God’s halo from the fresco, Chapel of the Scrovegni, painted by Giotto in Padua, analyzed with a capillary collimator located at the detector entrance

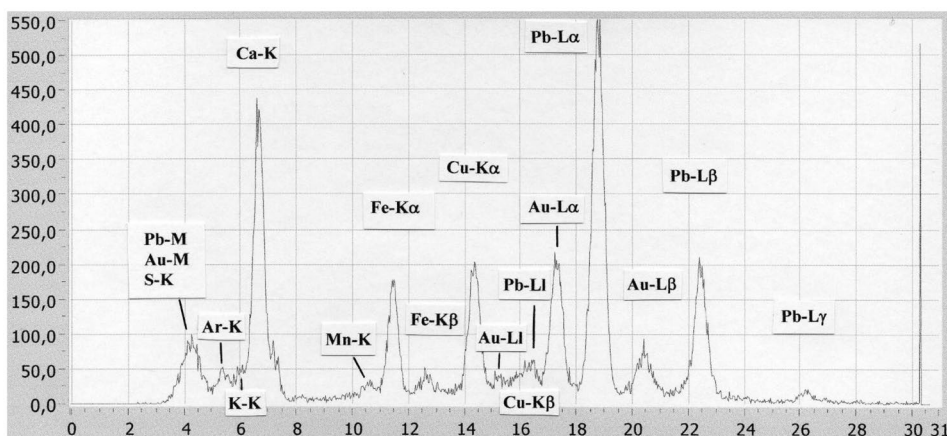


Fig. 11 Portable EDXRF equipment employed between 1995 and 2010 for analysis of ancient alloys, paintings, and frescos. The equipment is characterized by an Oxford-Amptek X-ray tube with Ag-anode, working at 30 kV and 100 μ A maximum voltage and current (red cylinder), and of a Si-PIN detector (rectangular box with cylinder). The MCA is incorporated in the detector box. A capillary collimator, produced by Institut für Gerätebau, was put on the detector entrance, when required. This image shows the EDXRF portable device during the analysis of a Moche pre-Columbian gold mask (Museum Royal Tombs of Sipán)



The third revolution occurred in the first years of this century and is related to the Si-drift X-ray detector (SDD), first proposed by Gatti and coworkers in the seventies constructed

by Longoni and Ketek scientists in the middle nineties [20, 21] and successively put in the market, first by Ketek and then by AMPTEK [12, 22] and by other companies.

Fig. 12 The most recent device for EDXRF-point analysis of paintings and metals. It is composed of a 40 kV, 100 μ A mini-X ray tube, a Si-drift detector with 135 eV energy-resolution at 6.4 keV, and a small PC. The MCA is incorporated in the detector box (123). A typical gold EDXRF-spectrum is shown in the PC

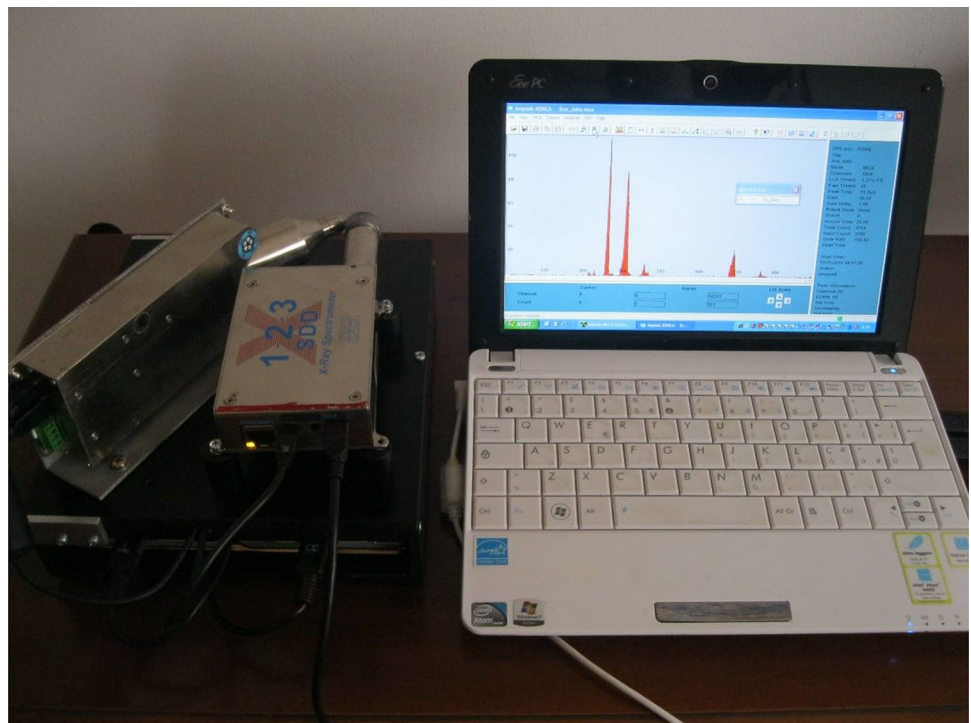


Fig. 13 Nose ornament PACEB-F4-00,032 (right) on gold and silver (right) and distribution of gold, silver, copper and mercury, as deduced from EDXRF-MA scanning (figures on the left)

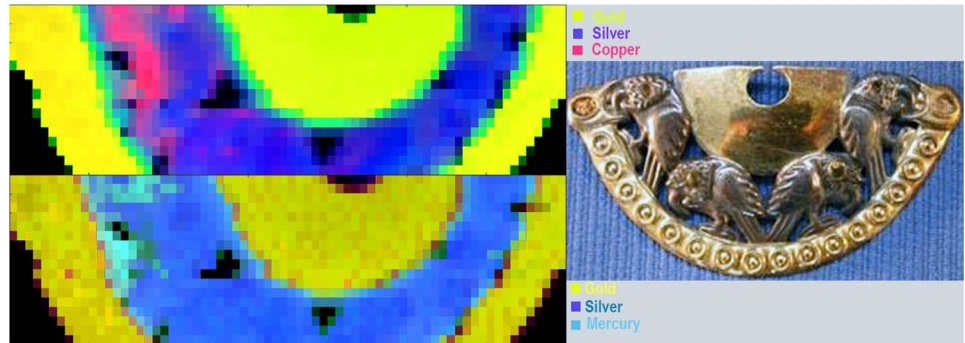


Fig. 14 Macro-scanning of the painting “La Fornarina” by Raphael; the measuring head is composed of a small-size X-ray tube working at 40 kV, 100 μ A, and two Si-drift detectors

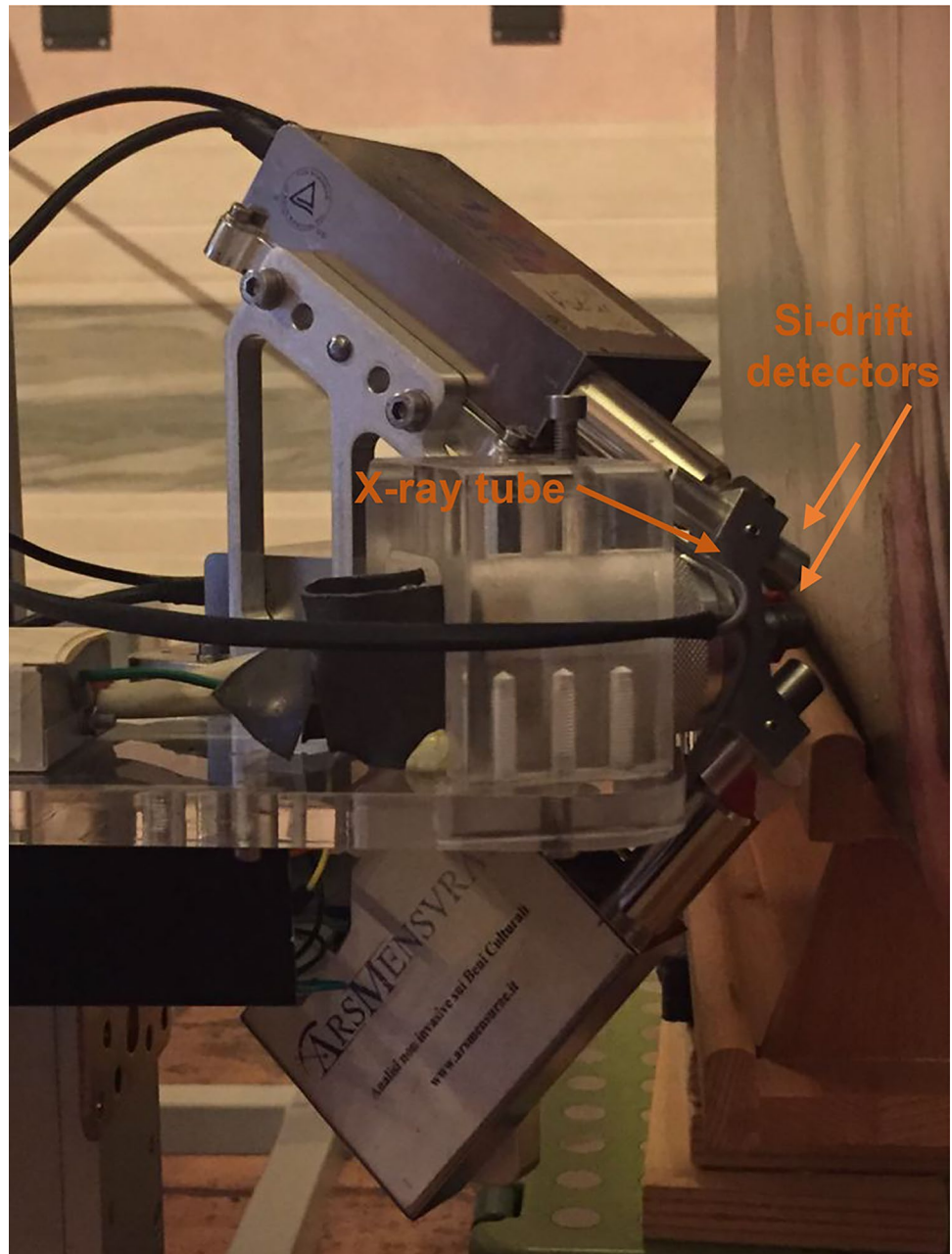


Fig. 15 **a** The painting “La Fornarina” by Raphael (painted in 1520 and located in the Galleria Nazionale di Arte antica, Palazzo Barberini, Roma); **b** the golden inscription RAPHAEL URBINAS on the left arm of the painting. The “gold” colored band at the border of the arm-band is not gold, but a Fe-based pigment, possibly yellow ochre: $\text{Fe}(\text{OH})_3$



Such a device was largely applied to study paintings [23, 24], frescos, gold, and silver, for example, pre-Columbian gold from the North of Peru [25, 26] (Fig. 11); gilded bronzes, for example a panel of the “Gate to Paradise,” a bronze door made by Lorenzo Ghiberti in Florence in 1425–1452 and brasses, such as the inscription on gilded brass at the top of the Trevi Fountain in Rome.

In the meantime, almost contemporaneously to the development of X-ray detectors, also dedicated and miniaturized X-ray tubes were developed (see Figs. 7, 8, 9, 11, and 12) [12, 27, 28], and small-size pulse-height analyzers (Figs. 7, 8, 9, 11, and 12), in such a manner that, currently, a complete equipment with X-ray tube and SDD-detector (including the MCA) can be assembled, with an energy resolution of the order of 130 eV at the $\text{Fe-K}\alpha$ line, a number of processed photons/s of the order of 10^5 and a weight of about 2 kg, including the PC or tablet (Fig. 12). Such a device allows to analyze areas of the order up to 0.01 mm^2 corresponding to diameter of about 0.1 mm.

All the described examples are related to point EDXRF analysis, i.e., the painting under study was analyzed in many points, generally according to areas of different color or composition. Finally, around 2010, the fourth revolution: a complete scan of a painting by Macro-XRF (MA-XRF) [29, 30] or μ -XRF (MA-XRF) [31]. A mechanical system is

required to this aim, to rapidly move the device in the plane of the object.

MA-XRF allows a visualization of the distribution of elements, obtained by scanning the surface of the painting with a focused or collimated X-ray beam of mm or sub-mm dimensions, according to the size of the painting. The method was first employed to test the homogeneity of a pre-Columbian nose ornament composed on gold and silver alloys (Fig. 13) and was then applied in the investigation of ancient paintings, as elemental distribution images can reveal hidden sub-surface layers, including modifications made by the artist (pentimenti) or restoration on the surface. In this way, it can provide a unique insight into the creative process of the artist and the painting’s conservation history. From that moment, scanning was largely prevailing over point analysis, in spite of the fact that, sometimes, long-time optimized point analysis can add additional information.

In February 2020, a second “scanning equipment” developed by us (Fig. 14) scanned “La Fornarina,” a famous painting by Raphael (Fig. 15) at the Gallery of Palazzo Barberini [32] Rome, during the exhibitions of the commemoration for 500 years after Raphael’s death. The results of the scanning are shown in Fig. 16.

Eventually, to handle the huge number of data, new sophisticated software had to be developed since the manual inspection

Fig. 16 Map of elements Pb, Hg, Sr, Cu, Fe, Mn as reconstructed from EDXRF-scanning

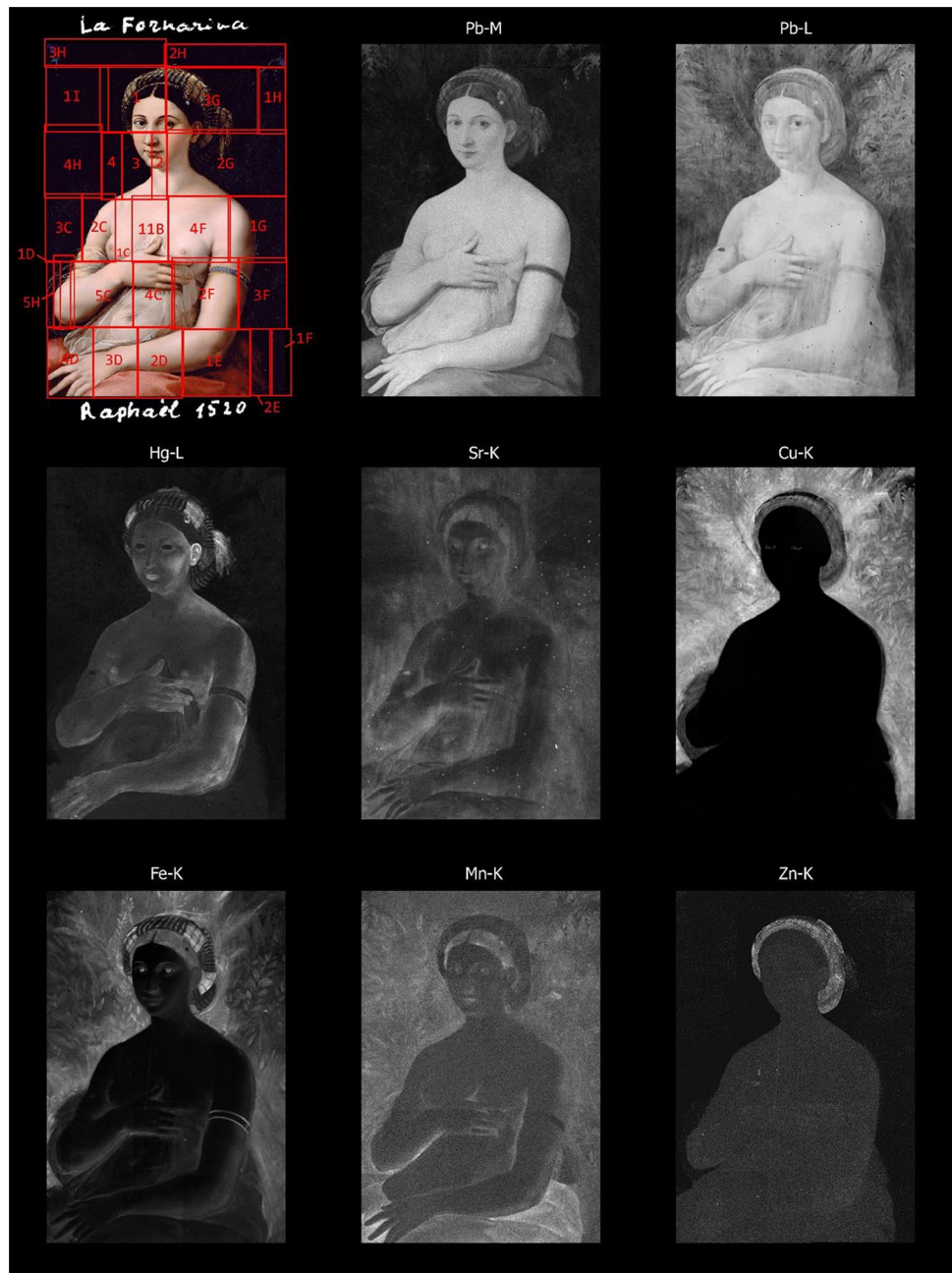


Fig. 17 Sergio Mascarenhas and Roberto Cesareo hugging the bust of Albert Einstein at the “Institute for Advanced Studies” of Princeton, in the summer of 1996



Table 1 Evolution of EDXRF-devices versus time, for analysis of paintings and metals

Years	X-ray source	Source characteristics	X-ray detector	Energy resolution (eV)	MCA
1971–1975 Figure 3	Radioisotopes (Pu ²³⁸ , Cd ¹⁰⁹ , Am ²⁴¹)	Low intensity and Flexibility	Proportional gas counter (Xe + CH ₄ , Kr + CH ₄), NaI	1000	LABEN 400 (heavy)
1972–1990 Figure 6	Radioisotopes	Big size and heavy X-ray tube	Si(Li) or HpGe	250	SILENA MCA MCA card
1985–1990 Figure 7	X-ray tube	Big size and heavy X-ray tube	Si(Li) or HpGe	200	MCA-card
1988–1996 Figure 8	Radioisotopes or X ray tube	Low intensity; heavy X-ray tube	HgI ₂	300	MCA-card or Pocket MCA
1995–1996 Figure 9	Ca-anode X-ray tube; Pd-anode X-ray tube (for S analysis)	Medium size X-ray tube	Si-PIN	200	SILENA MCA (medium wight)
1994–2008 Figure 11	Mini X-ray tube	Small X ray tube	Si-PIN	160	In the detector box
2008–2020 Figure 12	Dedicated Mini X-ray tube	Small X-ray tube	Si-drift	135	In the detector box
From 2008	Dedicated small size X-ray tube	Small, dedicated X-ray tube	Si-drift	135	In the detector box
From 2015	Dedicated and collimated small size X-ray tube *	Small, dedicated X-ray tubes	Si-drift* (2 or more)	135	In the detector box

*For scanning; movement in the plane of the painting (or object) is required

of millions of spectra would be impossible. This paves the way to a new and upcoming revolution. The digital revolution is where hardware has reached a miniaturization point where Software advancements are more advantageous, extracting the most information possible from the data available.

2 Conclusions

During the years, energy-dispersive X-ray fluorescence (EDXRF) proved to be the ideal technique to analyze artifacts of all type, and the corresponding EDXRF equipment has

had an impressive development during the last 50 years in all its instrumental components, as summarize in Table 1, i.e.,

- X-ray sources: from radioactive sources to big X-ray tubes to air cooled, small size, dedicated X-ray tubes
- X-ray detectors: from proportional gas counters to semi-conductor Si or Ge nitrogen cooled detectors to Peltier-cooled Si-drift detectors
- Pulse height analyzers: from big and heavy boxes to mini- electronic circuits incorporated in the detector box
- Also the measurement modality changed versus time: from single point analysis to a complete scanning of the object to be studied

3 A look to the future

The following evolutions may be expected in the next future for EDXRF analysis in archeometry:

- Miniaturized and dedicated X-ray tubes emitting a higher number of photons/s, allowing the scanning of a painting in μ -scanning mode and in a reasonable time
- Si-drift detectors thicker (up to a few mm) and with larger area, to improve the efficiency of the EDXRF-device
- A reliable software to process an enormous number of X-ray spectra, giving the relative intensity of all detected element and internal ratio (K and L-ratios)
- A possible complementary and “portable” technique (for example X-ray diffraction or Raman spectroscopy) able to deduce the molecules associated to the elements deduced from EDXRF

The final goal would be a complete reconstruction, point by point, of the pigments employed by the artist, and, therefore, of the painting itself.

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Declarations

Conflict of Interest The authors declare no competing interests.

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