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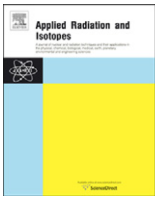

X-ray fluorescence in investigations of cultural relics and archaeological finds

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ABSTRACT

Some characteristic features of X-ray fluorescence (XRF) analysis make it an ideal method for investigations of cultural relics and archaeological finds. It has therefore become a standard method used in archaeometry. Paintings, frescos, manuscripts, pottery, metalwork, glass, and many other objects are analysed with the aim of recognising their materials, production technologies and origin, and for identifying counterfeits. This paper reviews various techniques used in XRF analyses of works of art, summarises the advantages and limitations of the method, and presents some typical examples of its use. The general review is supplemented by some techniques used and some results achieved at CTU-FNSPE in Prague.

1. Introduction

X-ray fluorescence analysis is based on Moseley's well-known law, discovered in 1913. The square root of the frequency v of the characteristic X-rays of a given series emitted by atoms is directly proportional to the proton number Z of the element:

$$\sqrt{\frac{v}{R}}=\frac{Z-S_n}{n} \tag{1}$$

R is the Rydberg constant, n is the principal quantum number of the corresponding electron shell (1 for the K-shell, 2 for the L-shell, etc.) and S_n is the screening factor, expressing the partial shielding of the orbital electrons in the outer shells from the charge of the nucleus by the negative charges in the inner shells (which is constant for a given shell).

E.g., for the K-series, this dependence can be rewritten approximately into the formula:

$$E_K \approx 1025(Z-1)^2 \tag{2}$$

where E_K is the photon energy (in eV). The author of this law, H.G.J. Moseley (1887–1915) would probably have been an outstanding candidate for the Nobel Prize if he had not been killed in the Battle of Gallipoli in the World War I.

An increase in the energy of characteristic X-rays with increasing proton numbers Z of elements allows various materials to be analysed from the viewpoint of their elementary composition, using X-ray emission. Elements contained in the material can be identified by the energies of the emitted characteristic photons. The concentrations of these elements can be determined from the intensities of the corresponding spectral lines.

Characteristic radiation can be excited by certain types of primary radiation, the choice depending on the purpose of the measurement and sometimes also on the equipment available in the laboratory:

- X-rays and gamma rays (XRFA—X-ray fluorescence analysis),
- protons and other heavy charged particles, usually from particle accelerators (PIXE—particle induced X-ray emission),
- electrons (EMP—electron microprobe, EPMA—electron probe microanalysis),
- synchrotron radiation.

As the basic principle is the same in all these cases, we will not give separate treatments to these related methods, which differ in principle only by the primary radiation sources, and we will summarise them in a single review.

XRF analysis is a universal analytical method, sensitive to most elements in the periodic system (excluding the lightest elements). XRF has been used successfully since the 1950s in industry and in many other branches of human activity. Some of its characteristic features make it an ideal method for investigations and material analyses of works of art and other cultural relics and archaeological finds (e.g., Ferreti, 2000; Milazzo, 2004). The non-destructiveness and non-invasiveness of the method (with some qualifications—see, e.g., Mantler and Klikovits, 2004) make XRF an irreplaceable tool for analysing valuable objects, when samples cannot be taken, surfaces must not be damaged, the substance of the materials must not be changed, etc. Moreover, the relatively easily transportable instrumentation allows measurements to be made in situ. Producers are making ongoing efforts to miniaturise XRF instruments. Microbeams employing capillary X-ray optics

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are another substantial improvement to the method, providing extremely high spatial resolution. For all these reasons, XRF has become a standard component of the whole spectrum of methods used in archaeometry. Paintings, frescos, manuscripts, pottery, metalwork, glass, and many other objects can be analysed with the aim of recognising their materials, their production technologies, their origin and trade routes, and also for identifying counterfeits. Precise knowledge of material composition is important not only from the general point of view of art history, but also for conservation and restoration works.

Many other analytical methods are used in parallel for investigating the materials of works of art and historic objects, e.g.:

- instrumental neutron activation analysis—INAA,
- atomic absorption spectroscopy—AAS,
- atomic emission spectroscopy—AES,
- inductively coupled plasma mass spectrometry—ICP-MS,
- accelerator mass spectrometry—AMS,
- X-ray absorption near-edge structure spectroscopy—XANES,
- Fourier transform infrared spectroscopy—FTIR,
- Mössbauer spectroscopy,
- metallography, petrography,
- Raman microscopy,
- scanning electron microscopy—SEM,
- "classical" chemical analytical methods.

One object is often analysed using several methods (see, e.g., Janssens and Van Grieken, 2004) that are complementary (e.g., some methods are sensitive to element contents, others to chemical compounds) or that allow cross checking of the results.

A huge number of investigations and papers have dealt with the use of XRF analysis in general, and specifically in archaeometry, and any review can only pick out typical characteristics of the issue and some representative and/or interesting examples. This limitation also applies to our paper.

2. Instrumentation

One of the major advantages of X-ray analysis is the possibility of making non-destructive and in situ measurements. Development has therefore focused on miniaturising the measuring devices for portable and hand-held analysers (see, e.g., Janssens and Van Grieken, 2004; Gigante et al., 2005; Potts and West, 2008). However, a number of art objects and archaeological finds can be transferred to the laboratory, and laboratory analysers with their higher resolution and greater sensitivity also maintain their place.

The "traditional" arrangement of an XRF device with an X-ray tube or a sealed radionuclide source (^{55}Fe, ^{238}Pu, ^{241}Am) as the primary radiation source produces X-ray beams with diameters of the order of a few mm. This means that the traditional arrangement is well applicable to larger objects such as metal sculptures and applied art products, uniform areas of pigments in frescos, ceramics, etc., but it is not suitable for investigations of small objects, such as pigments on miniature paintings or small decorations. However, miniature X-ray tubes have been developed which, in combination with polycapillary X-ray optics, enable the X-ray beam to be focused to the order of tens of micrometres, and they are able to solve this limitation. Collimating the beam in a small spot is one of the advantages of higher radiation fluxes from X-ray tubes compared with radionuclide sources, where strong collimation prolongs the measurement time to an unacceptable extent.

Hand-held devices (some of them weighing less than 1.5 kg) are now produced commercially by several producers (this review will not cite booklets and other publications issued by commercial companies for advertising purposes). They typically use a miniature X-ray tube with voltage up to about 40–50 kV as a source of primary radiation. In a few cases, a radionuclide source is also an option. For light elements, voltages of about 10 kV are used, and the voltage is increased with increasing proton number of the analysed elements. An X-ray tube with voltage 40 kV with a tungsten anode is capable of measuring elements from K to Ba from their K-lines, and can measure higher Z elements up to uranium from their L-lines.

Characteristic X-rays are usually detected by a semiconductor thermoelectrically cooled detector. "Traditional" liquid nitrogen cooled Ge or Si detectors have been replaced by small HgI_2, Si-PIN, Si-drift or CZT (cadmium–zinc–telluride) detectors. These small detectors are cooled to about $-30\,^{\circ}$C by means of a Peltier circuit, and have high spectrometric resolution (for silicon-based detectors about 150 eV at 5.9 keV, CZT about 300 eV).

The range of measurable elements extends in the optimal case from Na to U, but most usually the lower detection threshold is at higher proton number elements than Na (Mg, Si, sometimes even S). The detection limits for most elements are in the order of tens ppm, but for light elements they increase up to the order of hundreds ppm. In general, detecting the lightest elements is a common problem of XRF measurements due to the low energy of the characteristic X-rays, which are effectively absorbed by any layers of materials between their place of origin and the detector, including the air.

Laboratory XRF spectrometers are designed to maximise measurement sensitivity and measurement accuracy; they can be used for samples of materials (in this case they lose one of the main advantages of XRF—non-destructiveness) or for transportable objects. They usually use an X-ray tube, exceptionally a radionuclide, as a primary source, and work in the wave-dispersive mode (WDXRF—based on changes in the diffraction angle of X-rays with changing wavelength) or in the energy-dispersive mode (EDXRF—based on spectrometry of the energies of X-rays, usually by a semiconductor detector). The same is valid for some larger, but still portable spectrometers. For example, Lutz and Pernicka (1997) state a detection limit of 0.006–0.01 wt% for their portable EDXRF spectrometer and for elements from the middle of the periodic table (Ag, Sn, Sb).

In contrast to XRF, where the X-ray tube or a radionuclide source can be transported and measurements can be carried out in situ, PIXE is connected with an accelerator laboratory and an alpha emitting radionuclide is used only in exceptional cases. The most frequent bombarding particles are protons in the energy range of about 1–4 MeV. The first experiments using a Van de Graaff accelerator were carried out in the early 1970s (Johansson and Johansson, 1976). The short range of the protons in the material gives preference to measuring samples in a vacuum, although in recent years experiments and measurements in the air have also appeared. The short range of the bombarding particles also means that only a thin surface layer (10–15 μm) is effectively analysed. A significant contribution to reducing the threshold of detection and increasing accuracy is the lack of background Compton scattering, which always exists as a disturbing effect when irradiating with photons. The PIXE lower detection limit is thus usually one or two orders of magnitude below the detection limit for XRF excited by photons. Proton beams can be focused on a diameter of the order of μm, and thus a detailed microanalysis can be carried out.

The electron microprobe is most often associated as additional equipment with an electron microscope. An electron beam irradiates sample volumes typically of 10–30 μm^3, sometimes even less; the detection limit for modern instruments is in tens of ppm.