X-RAY FLUORESCENCE (XRF) SPECTROMETRY

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COSCH Case Studies that have employed this technology: Roman coins, Germolles

Definition

XRF spectrometry is a non-destructive analytical technique widely used to determine the elemental composition of materials. It has been demonstrated to be effective in fields including biology, medicine, geology, material science, environmental studies, and cultural heritage, among many others. The suitability of this technique for conducting elemental surveys that require no extraction of samples makes it very versatile in cultural heritage research.

Description

X-ray fluorescence is induced when photons with enough energy, emitted from an X-ray source, interact with a material. High-energy photons induce ionization of inner shell electrons through the photoelectric effect, creating electron vacancies in these shells. These vacancies are almost immediately filled with electrons from outer shells resulting in emission of fluorescent radiation, which is characteristic for each element. The lines observed in the XRF spectrum enable identification of the chemical elements present. XRF analysis is therefore a powerful analytical tool for the spectrochemical characterization of most elements present in an object.

An XRF spectrometer contains several components including: an excitation source or X-ray tube, a sample chamber or open shutter system to deliver X-rays to the sample, a detector to determine the characteristic X-rays generated, an analyser that converts the measured energies to their correspondent electronic transitions, and a display device to visualize the measured spectra. Early XRF instruments contained a sample chamber, typically of limited size, that allowed only for the measurement of samples extracted from cultural heritage objects. In response to the needs of heritage scientists, modern instruments employ open beam systems that allow simultaneous X-ray irradiation and detection of fluorescence emitted by actual historic objects of all sizes without requiring sampling. The detector is composed of two charged electrodes that have a non-conducting or semi-conducting material positioned between them. The X-rays ionize these materials causing them to become conductive. The unbound electrons are accelerated toward the detector anode to generate a signal that can be measured. Based on the detector used, X-ray techniques can be divided into energy (EDXRF) and wavelength dispersive (WDXRF).

Two types of analysis are possible in XRF. Qualitative analysis allows identification of the elements present in the object, and has been used on paper artworks, paintings, and ceramics. Quantitative analysis involves the determination of the relative amount of each element present in an object. Since the material must be infinitely thick to X-ray penetration, the number of heritage objects that can be quantitatively analysed is very limited. Typically, we consider the "infinite thickness" of a sample as the thickness from which 99 per cent of the intensity of a given element (analyte) is collected. The thickness of a material can only be estimated for values lower than this limit. It is important to notice that this infinite thickness depends on the X-ray penetration and absorption. For this reason when performing quantitative analysis it is better to consider the higher energy/ penetration lines for a given element. In the case of silver, a K line has an approximate penetration of 100 microns while the L (lower energy) penetrates to about 10 microns. Therefore, the signal arising from the layer of higher penetration (K line) is used. Quantitative analyses are typically conducted on metal objects and the results are usually expressed in weight percentage of detected elements. However, it is important to emphasize that XRF is a surface technique and factors such as non-homogeneity, enrichment, and corrosion can lead to results that can deviate significantly from quantities in the bulk. Generally, the original composition of a historic metallic object can be determined by studying the composition of the bulk. This typically requires extraction of samples or the use of destructive analytical techniques. Therefore, when using surface methods such as XRF the information could be limited to the first micro-layers of the object.

XRF reports typically include the instrumental parameters and spectrometer model used, the elements detected, the level of confidence, the elemental concentration (if applicable), the calibration method used, and the estimated error. The use of synchrotron radiation and scanning systems (macro-XRF) are relatively recent developments that have provided great advances in the cultural heritage field. Most cultural institutions use XRF spectrometry together with complementary techniques such as Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), and most recently multispectral (MSI) and hyperspectral imaging (HSI) techniques.

Significant Applications

Early investigations involving the use of XRF for analysing cultural heritage materials date back to the 1950s. The work of Kraay (1958) on the determination of the composition of electrum coinage offers a good example of innovation in applying the technique to numismatic research at that time. More recently, Linke et al. have made significant advancements in the application of XRF to the study of numismatic collections. The authors evaluated the advantages and limitations of the technique when conducting qualitative analysis of metal alloys and also described surface effects that can lead to misinterpretation of the results. Special attention has been paid to silver surface enrichment effects observed in historic coins made of silver-copper alloys (Linke et al. 2004). Although small objects such as coins can be easily transported to the laboratory, this is not always the case for larger objects whose movement may be restricted. Therefore, the cultural heritage field has benefited from a series of technological developments in XRF spectrometry that have taken place over the past years. The development of portable XRF instruments that make use of thermoelectrically-cooled detectors and miniaturized X-ray tubes has resulted in broader applications of the technique to study a larger range of objects. These developments have had a significant impact in archaeological and art-technological research conducted either in the laboratory or on site. Nowadays, XRF spectrometry has become a standard analytical tool in museums, research institutes, and universities.

Important applications in the field of archaeological research include: soil analysis for evidence of human activities (Pastor et al. 2016), sourcing of obsidian and other lithic materials (Craig et al. 2007; Frahm 2014), study of ceramics (Pincé et al. 2016), and identification of pigments (Shoval and Gilboa 2016). However, several controversial issues regarding the interpretation of XRF results in archaeological research have been highlighted recently. For example, the use of the technique for obsidian sourcing has been a subject of debate among researchers (Frahm 2013; Speakman and Shackley 2013). The scepticism has arisen because a group of researchers believe that the results have low accuracy and precision, and that calibration and correction factors have been wrongly applied. There have also been claims that researchers show little knowledge about fundamental XRF issues such as sample size restrictions and morphology effects (Frahm 2013). On the other hand, Speakman and Shackley (2013) point out that their critics do not take into consideration the importance of following standard analytical protocols in order for the results to be verifiable by other researchers. This is a subject of ongoing debate and further research and discussion will help to advance the field of archaeometrical analysis.

In the art technological field, XRF has undergone a significant evolution as a result of the integration of scanning devices. Macro-XRF instruments are increasingly employed in cultural and research institutions to scan the surface of large 2D objects. In this respect, the work of Alfeld can be considered pioneering due to the development of the first XRF scanner used for visualization of hidden paint layers. These instruments are capable of imaging the distribution of the main elements present in surface and subsurface paint layers. The interesting visualization of underpainting in a work by Rembrandt van Rijn using macro-XRF were reported by Alfeld et al. (2013). The authors demonstrated that this approach can be quite promising in situations where neither infrared reflectography nor neutron induced autoradiography can be used as visualization tools for revealing underpainting.

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