

Basic Theory of X-ray Fluorescence

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X-ray Fluorescence Introduction

Although X-ray fluorescence spectroscopy is no longer regarded as a new instrumental technique for elemental analysis, on-going evolutionary developments continue to redefine the role of this important analytical tool. From the demonstration of the first principles in the 1960s to the development of the first commercial instruments in the 1970s, the increasing availability of affordable computational power has at least been as important to the desirability and acceptance of the technology as innovative hardware design. With the widespread availability and use of a 32-bit microprocessor personal computer as the industry standard platform, X-ray fluorescence spectroscopy has become a useful and complimentary laboratory tool to other techniques.

X-Ray Fluorescence Theory

An electron can be ejected from its atomic orbital by the absorption of a light wave (photon) of sufficient energy. The energy of the photon ($h\nu$) must be greater than the energy with which the electron is bound to the nucleus of the atom. When an inner orbital electron is ejected from an atom, an electron from a higher energy level orbital will be transferred to the lower energy level orbital. During this transition a photon may be emitted from the atom. This fluorescent light is called the characteristic X-ray of the element. The energy of the emitted photon will be equal to the difference in energies between the two orbitals occupied by the electron making the transition. Because the energy difference between two specific orbital shells, in a given element, is always the same (i.e. characteristic of a particular element), the photon emitted when an electron moves between these two levels, will always have the same energy.

Therefore, by determining the energy (wavelength) of the X-ray light (photon) emitted by a particular element, it is possible to determine the identity of that element.

For a particular energy (wavelength) of fluorescent light emitted by an element, the number of photons per unit time (generally referred to as peak intensity or count rate) is related to the amount of that analyte in the sample. The counting rates for all detectable elements within a sample are usually calculated by counting, for a set amount of time, the number of photons that are detected for the various analyte characteristic X-ray energy lines. It is important to note that these fluorescent lines are actually observed as peaks with a semi-Gaussian distribution because of the imperfect resolution of modern detector technology.

Therefore, by determining the energy of the X-ray peaks in a sample's spectrum, and by calculating the count rate of the various elemental peaks, it is possible to qualitatively establish the elemental composition of the samples and to quantitatively measure the concentration of these elements.

Importance of Sample Preparation

Sample preparation is by far the most important step in any analytical technique. How well the sample is prepared and presented will affect the ability to yield accurate data from the instrument. X-ray fluorescence is not immune to this crucial step, despite the ability to correct for standard counting errors, instrument variation errors, operation errors, and matrix effects. Choosing the right sample preparation technique will depend on the goals of accuracy and precision the analyst needs or wishes to attain.