History of X-ray Spectroscopy

Written by Skyray Instruments

X-rays were first discovered by Wilhelm K. Roentgen (German physicist, 1845-1923) who won the Nobel Prize in 1901, for the discovery of x-rays. X-rays have been used for commercial elemental analysis since the 1950’s. X-ray spectroscopy is much older than that, dating back to 1909 when Charles G. Barkla found a connection between x-rays radiating from a sample and the atomic weight of the sample. In 1913, Henry Gwyn Jeffreys Moseley helped number the elements with the use of x-rays, by observing that the K line transitions in an x-ray spectrum moved the same amount each time the atomic number increased by one. He is credited for changing the periodic tables which were based on increasing atomic weight, to periodic tables based on atomic number. He later laid the foundation for identifying elements in x-ray spectroscopy by establishing a relationship between frequency (energy) and the atomic number.

The potential of the technique was quickly realized, with half of the Nobel Prizes in Physics given to the development in x-rays from 1914 to 1924. Originally x-ray spectroscopy used electrons as an excitation source, but the requirements such as a high vacuum, electrically conducting specimens, and volatility of the sample posed major roadblocks. To overcome these problems an x-ray source was used to promote the fluorescent emission in the sample. Excitation of the sample by this method introduced roadblocks of its own, by lowering the efficiency of photon excitation and requiring instrumentation with complex detection components. Despite these disadvantages, the fluorescent emission of x-rays would provide the most powerful tool for the analyst using commercial instruments.

Development of the Commercial X-Ray Spectrometers

Four types of spectrometers are available to the analyst. From the 1950 to 1960 nearly all the x-ray spectrometers were wavelength dispersive spectrometers. In a wavelength dispersive spectrometer, a crystal separates the wavelengths of the fluorescence from the sample, similar to grating spectrometers for visible light. The other x-ray spectrometer available at that time was the electron microprobe, which uses a focused electron beam to excite x-rays in a solid sample as small as $10^{-12}$ cm$^3$. The first microprobe was built by R. Castaing in 1951 and became commercially available in 1958. In the early 1970′s, energy dispersive spectrometers became available, which use Li-drifted silicon or germanium detectors. The advantage these instruments brought was the ability to measure the entire spectrum simultaneously. With the help of computers, deconvolution methods can be performed to extract the net intensities of individual x-rays.