

X-Ray Fluorescence Analysis

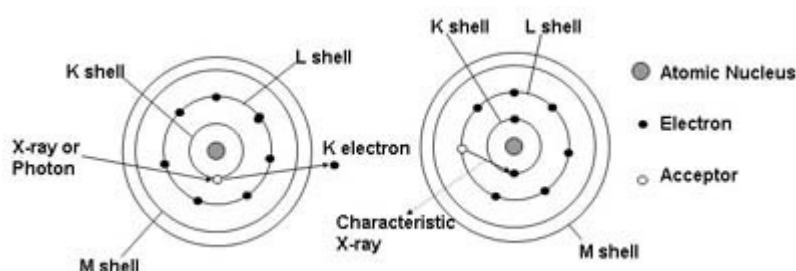
► 1-1. Descriptions

Here we introduce the principle and application examples of X-ray fluorescence.

1. Principle

X-ray is a type of electromagnetic waves such as visible light ray, but the key difference is its extremely short wavelength, measuring from 100Å to 0.1Å. And compared to normal electromagnetic waves, X-ray easily passes through material and it becomes stronger as the material's atomic number decreases. X-ray fluorescence analysis is a method that uses the characteristic X-ray (fluorescent X-ray) that is generated when X-ray is irradiated on a substance. The fluorescent X-ray is the excess energy irradiated as electromagnetic field, which is generated when the irradiated X-ray forces the constituent atom's inner-shell electrons to the outer shell and the vacant space (acceptor) falls on the outer-shell electrons. The generation of fluorescent X-ray is shown in Figure 1. These rays possess energy characteristic to each element, and qualitative analysis using Mosley's Equation and quantitative analysis using the energy's X-ray intensity (number of photons) are possible.

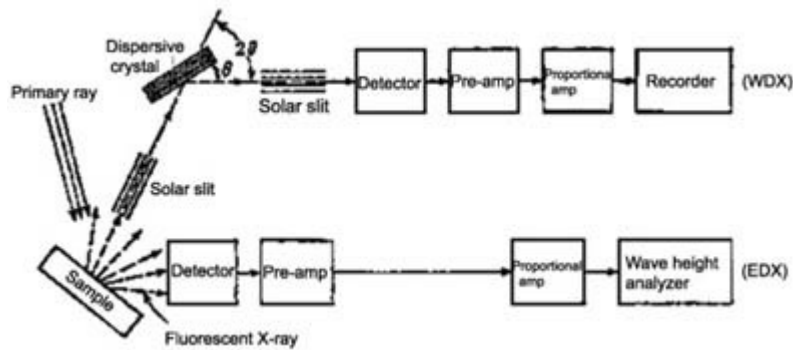
X-ray fluorescence analysis can be considered as spectrochemical analysis of an X-ray region. It has the same characteristics as atomic absorption spectrometry and optical emission spectrometry which conduct measurement by putting the sample into solution. For example, in flameless atomic absorption spectrometry (FLAAS), elements in the sample are atomized in 2000 to 3000C flame and in ICP atomic emission spectrometry (ICP-AES), sample is excited in 6000 to 9000C plasma flame. X-ray fluorescence likewise excites the sample using X-ray to obtain information.



(Figure 1 X-ray generation)

2. Device Structure.

X-ray fluorescence analysis devices can be largely categorized into wavelength-dispersive X-ray spectroscopy (WDX) and energy-dispersive X-ray spectroscopy (EDX). (Shown in Figure 2.) WDX disperses the fluorescent X-ray generated in the sample using dispersion crystal and measures it using a goniometer, resulting in a large size. On the other hand, the detector in EDX has a superior energy resolution and requires no dispersion system, which enables downsizing of the device.

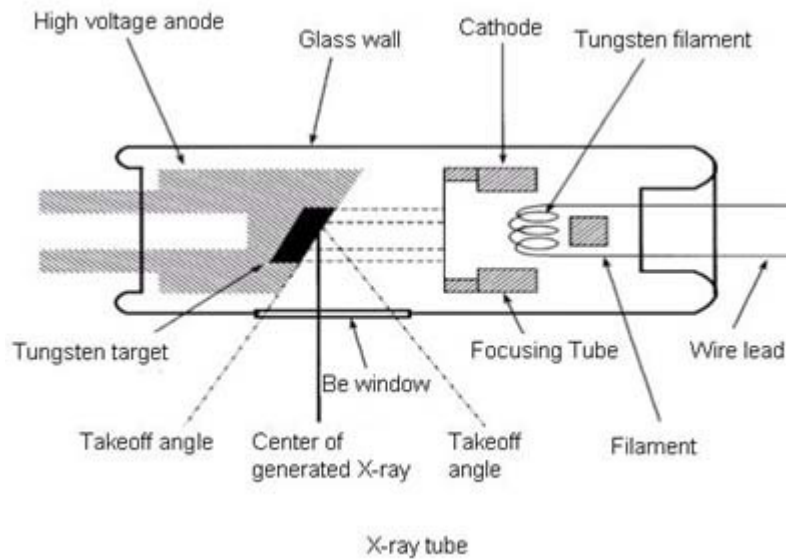


(Figure 2 WDX and EDX types)

2-1 X-Ray Generation

X-ray is generated when the X-ray tube (Figure 3) accelerates the electrons at high voltage and bombards them against the metal anode (anti-cathode). There are two types of X-ray tubes, side window type and end window type, and both are designed to irradiate intense X-ray on the sample surface as evenly as possible.

Beryllium foil is commonly used for the window for retrieving the incident X-ray. For the anti-cathode, (sometimes referred as "target") tungsten, rhodium, molybdenum and chrome are used. These anti-cathode are chosen based on the analysis sample. X-ray tubes with anti-cathode similar to analysis element are essentially not used.

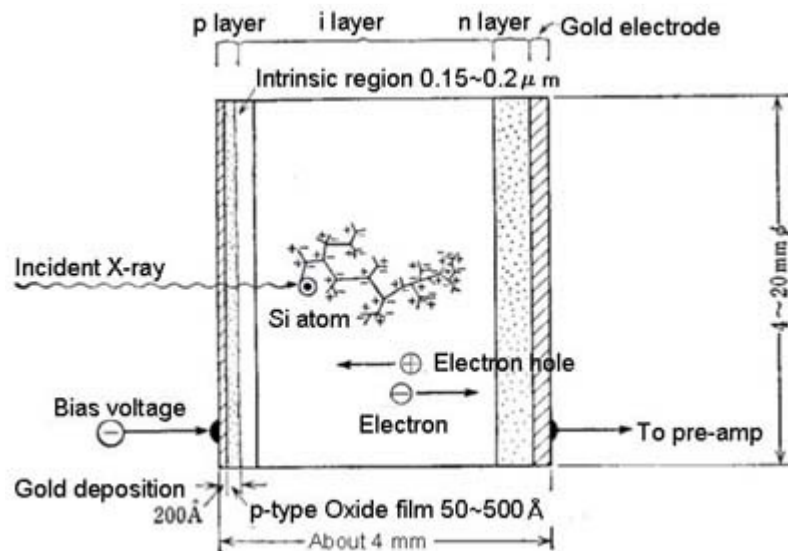


(Figure 3. X-ray tube bulb)

2-2 Detector

Figure 4 shows the basic structure of a Si (Li) device. Si (Li) device features a p-i-n+ structure diode. Diode can only pass electric current in one direction (rectification mechanism). When voltage is applied against the current (reverse bias) and light enters in this state, the electrons in the forbidden band are excited into conductive band and only the current for the excited electron travel. For X-ray detection, each current pulse corresponding to an incident X-ray photon is measured one by one. The instantaneous current value of a single pulse is relative to the incident X-ray energy, so X-ray energy can be found by measuring the wave height of the current pulse.

Si (Li) semiconductor detector is a diode with Li spread over high-purity single Si crystal, diameter 3 to 6mm and thickness 3 to 5mm, cooled with field-effect transistor and liquid nitrogen and maintained in vacuum. When semiconductor detector was first developed, damage caused by application of high voltage that resulted from shortage of liquid nitrogen and consequent temperature rise, was reported. With current devices, the surface temperature of the detector is monitored and when it rises above a certain temperature, protection circuit shuts off the high voltage to the detector, eliminating damage to the detector from accidentally applying high voltage. At low frequency of use, it can be used about 30 minutes after supplying it with liquid nitrogen.



(Figure 4. Si (Li) device structure)

2-3 Sample Chamber & Measurement Atmospher

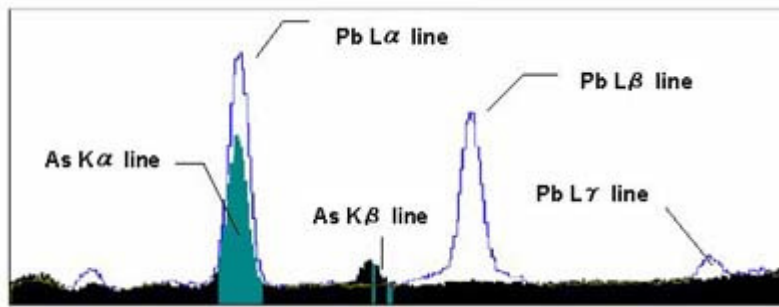
There are two types of sample chambers, top-surface irradiation type that irradiate X-rays from above, and bottom-surface irradiation type that irradiate from below. There are not many differences between the two types in detection concentration, but for sample observation and measurements conducted while moving the stage, the top-surface irradiation is better.

In most devices, atmosphere in sample chambers can be decompressed. This is because X-rays are absorbed and lose intensity in atmosphere. For light element measurements, setting the measurement atmosphere is vital.

2-3. Qualitative Analysis

In defining X-ray fluorescence analysis, the wavelength of the characteristic X-ray or the regularity of the energy and atomic number are used. Most devices are equipped with the automatic identification (definition) feature but it is important to note various interfering spectrums.

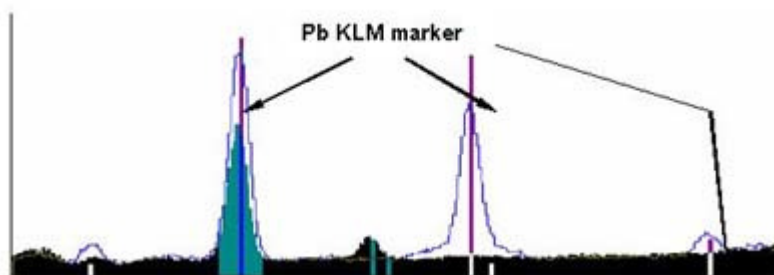
Depending on the element types contained in the sample, energy position of characteristic X-rays may be close to each other or spectrums may overlap. Figure 5 shows an example with As and Pb spectrums.



(Figure 5 As and Pb Spectrums)

As shown above, if Pb is contained in the sample, the energy position of As's $K\beta$ line overlap with Pb's $L\beta$ line, and would lead to identifying As by mistake. There are multiple characteristic X-rays of an element, such as $K\beta$ line, $K\alpha$ line, $L\beta$ line, $L\alpha$ line etc.

In cases such as this, confirmation with a KLM marker shown in Figure 5 is necessary. A KLM marker compares the intensity and theoretical energy positions of multiple characteristic X-rays. Figure 6 shows an example with the KLM marker of Pb displayed on the spectrum.



(Figure 6. Pb KLM marker)

The X-ray intensity of Pb is shown and if the sample contains Pb, a peak would be present at each energy position at about the same interval as the KLM marker. If peaks are not present at Pb energy positions other than Pb's $L\beta$ line, it can be judged that Pb does not exist in the sample. Likewise, if peaks do not exist on the As's $K\beta$ line as well as the $K\alpha$ line, the sample does not contain As. As above, by displaying the KLM marker and observing the intensity comparison of multiple characteristic X-rays, qualitative analysis can be performed accurately.

2-4. Quantitative Analysis

The following is an overview of conducting quantitative analysis using fluorescent X-ray.

When a sample that contains element A is irradiated primary X-ray, fluorescent X-ray of element A is generated, but the intensity of this fluorescent X-ray is dependent on the amount of element A in the sample. The more element A contained in the sample, the higher the intensity of the fluorescent X-ray that is generated. Taking this into account, if the fluorescent X-ray intensity and concentration of an element contained in a sample is known, then we can go in reverse and find how much element A contained in another sample by its fluorescent X-ray intensity.

When conducting quantitative analysis with fluorescent X-ray, there are two basic methods. The first is to create a standard curve. This method involves measuring several samples with a known element concentration, and finding the relationship between the intensity of the measured element's fluorescent X-ray and the concentration. By referring this relationship, element concentration of unknown sample is obtained only with information on its fluorescent X-ray intensity.

The other method is known as the fundamental parameter method of theoretical calculation, or the FP method. With this method, if the type and properties of all elements that compose a sample are known, then the intensity of each fluorescent X-ray can be derived theoretically. By utilizing this method, the composition of unknown sample can be extrapolated by its fluorescent X-ray intensity of each element.

3. Conclusion

Since X-ray fluorescence analysis can analyze a sample non-destructively and quickly, it can be applied to a wide range of use such as manufacturing and quality control. Recently, as techniques for high-sensitivity, technologies such as filtering and lamination have been applied to eliminate the interference of background, which made measurement of trace amounts possible. This analysis method will become more widespread particularly in measurements of hazardous metals in materials and soil.