X-ray Fluorescence

Objectives: This experiment introduces the method of x-ray fluorescence (XRF). You will use a portable XRF system to determine the concentration of silver in a sample by direct measurement and from the attenuation of x-rays produced in a copper backing.


X-ray fluorescence is one of the most widely used analytical methods for the qualitative identification of elements with atomic number greater than 8, and is widely used for the quantitative measurement of elements in thin samples such as filters. Multi-element measurements can be made within a few minutes and the method is non-destructive. XRF systems have many commercial applications, including the analysis of alloys, soils, liquids and paint films. One disadvantage is that for most elements the sensitivity is limited to ppm concentrations. Detection and measurement also become progressively worse as the atomic number of the element decreases because Auger electron emission competes more significantly with fluorescence.

When atoms in a sample are bombarded with electrons, photons or ions, inner shell electrons get ejected. When an excited ion returns to the ground state by transitions involving electrons from higher energy levels, it emits characteristic x-rays (fluorescence). In an energy-dispersive XRF system, the x-rays from the various excited ions are detected with a semiconductor detector (see Figure 1).

Figure 1. Basic components of an energy-dispersive x-ray fluorescence system
The result is an x-ray spectrum similar to that acquired in gamma-ray spectrometry (see Figure 2). The peaks labeled K\(_{\alpha}\) and K\(_{\beta}\) result from higher energy electrons in lead ions releasing energy as they move to a vacancy in the n=1 energy level. The L\(_{\alpha}\), L\(_{\beta}\) and L\(_{\gamma}\) peaks result from similar electron transitions to a vacancy in the n=2 energy level.

![X-Ray Fluorescence of Lead from \(^{109}\)Cd](image)

Figure 2. Energy-dispersive x-ray fluorescence spectrum of sample containing lead

The portable XRF system you will be using contains 3 radionuclides (\(^{55}\)Fe, \(^{109}\)Cd and \(^{241}\)Am) that can serve as the excitation source. The \(^{55}\)Fe and \(^{109}\)Cd sources decay by electron capture, emitting x-rays of 5.9 keV and 22.1 keV, respectively. \(^{109}\)Cd also emits an 88-keV gamma ray that can be used for excitation. \(^{241}\)Am undergoes alpha decay which is accompanied by the emission of a 59.5-keV gamma ray. These sources are used to selectively excite different elements in the sample being analyzed. In this experiment, silver will be measured using the \(^{241}\)Am source, while \(^{109}\)Cd will be used to analyze for copper.

Consider a sample consisting of a copper plate coated with a thin layer of silver. If this sample is exposed to an appropriate excitation source, copper fluorescence as well as emissions from the silver layer will be produced. The copper x-rays reaching the detector will be attenuated by the silver layer and the copper fluorescence signal intensity will be a function of the silver layer thickness; the thicker the layer, the more attenuation and the lower the signal intensity. The silver layer thickness can be determined from a calibration curve based on the copper x-ray signal intensity as a function of varying silver layer thickness. In this experiment, the unknown sample consists of a dispersion of silver in a low atomic number matrix. It is assumed that the principal attenuation of the x-rays originating from a copper backing will be due to the presence of the dispersed silver.

**BEFORE COMING TO LAB:** Calculate the copper fluorescence signal for a copper plate covered with a layer of silver having a thickness of 300 \(\mu\)g/cm\(^2\). Assume the unattenuated copper signal is 8700 and the mass attenuation coefficient (\(\Sigma\)) for the 8-keV copper x-rays in silver is 216 cm\(^2\)/g.
PROCEDURE

A. Direct Determination of Silver Concentration

The instructor will demonstrate the use of the NITON 701 XRF spectrum analyzer. Carefully note all steps in the analysis procedure and all safety cautions. First, you will calibrate the instrument by analyzing silver standards that were prepared by depositing a known amount of silver on a Mylar backing. Plot the analyzer signal as a function of $\mu g \text{ Ag/cm}^2$ for the standards and fit the data with a linear least-squares line. Care must be taken when working with the silver standards. **Wear gloves when handling the standards and be careful not to touch the silver deposit.** Analysis of an unknown sample will be made and the silver content of the unknown will be determined from the analyzer signal and interpolation of the calibration curve.

B. Indirect Determination of Silver Concentration

The unknown sample will also be analyzed for silver by monitoring the attenuation of the x-rays from a copper plate placed behind the sample when excited by $^{109}\text{Cd}$. First, determine the copper signal associated with the sample itself (no backing), and again with the copper plate as a backing. Then measure the copper signal directly from the copper plate. Finally, monitor the copper signal as different silver thicknesses are placed over the copper plate. Plot $\ln$ of the copper signal as a function of the silver layer thickness ($\mu g \text{ Ag/cm}^2$) and fit the data with a linear least-squares line. Determine the unknown sample silver concentration by interpolation of the calibration curve. Compare this result with that from the direct determination. Comment on what factors might account for any observed differences.