X-Ray Fluorescence analysis (XRF)

X-Ray Fluorescence analysis (XRF) is a nondestructive physical method used for chemical elemental analysis of materials in the solid or liquid state. The specimen is irradiated by photons or charged particles of sufficient energy to cause its elements to emit (fluoresce) their characteristic x-ray line spectra. The detection system allows determining energies of the emission lines and their intensities. Elements in a specimen are identified by their spectral line energies or wavelengths for qualitative analysis, and intensities are related to concentrations of elements providing opportunity for quantitative analysis. Computers are widely used in this field, both for automated data collection and for reducing the x-ray data to weight-percent and atomic-percent chemical composition or area-related mass.

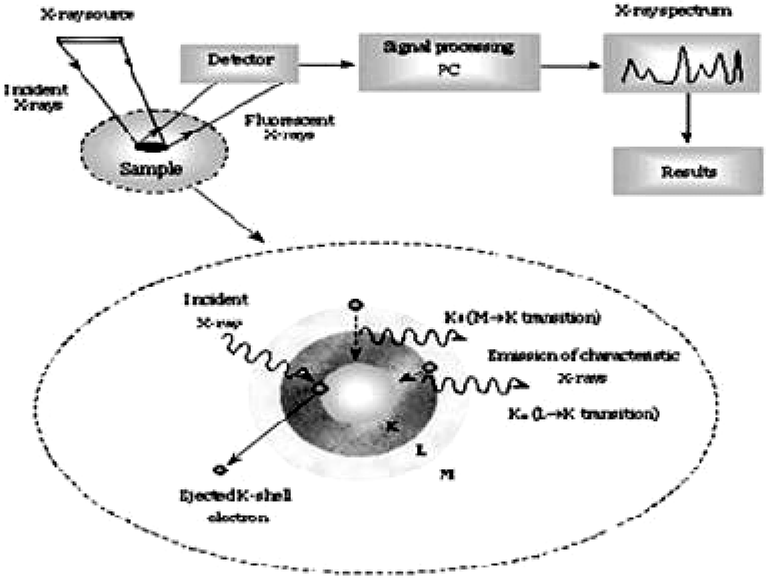

Figure 1. The principle of XRF and the typical XRF detection arrangement.

When a primary x-ray from an x-ray tube or a radioactive source strikes a sample providing excitation, the x-ray can either be absorbed by the atom or scattered through the material. The process in which an x-ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the "photoelectric effect." During this process, if the primary x-ray had sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies lead to an instability of the atom. As the atom returns to its stable state, electrons from the outer shells are transferred to the inner shells and in the process give off a characteristic x-ray which energy is determined by the difference between the two binding energies of the corresponding shells. All elements emit X-rays at their own characteristic energies. These X-rays are called "K lines" if they are emitted by an electron filling the innermost shell called K, and "L lines" if they result from filling the next electron shell, the L shell. Sometimes, as the atom returns to its stable condition, instead of emitting a characteristic x-ray it transfers the excitation energy directly to one of the outer electrons, causing it to be ejected from the atom. The ejected electron is called an

"Auger" electron. This process is a competing process to XRF. Auger electrons are more probable in the low Z elements than in the high Z elements. Because each element has a unique set of energy levels, each element produces x-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The process of emission characteristic x-rays is called "X-ray Fluorescence," or XRF. Analysis using x-ray fluorescence is called "X-ray Fluorescence Spectroscopy." In most cases the innermost K and L shells are involved in XRF detection. A typical x-ray spectrum from an irradiated sample will display multiple peaks of different intensities. X-ray energy spectrum is shown in Fig. 2.

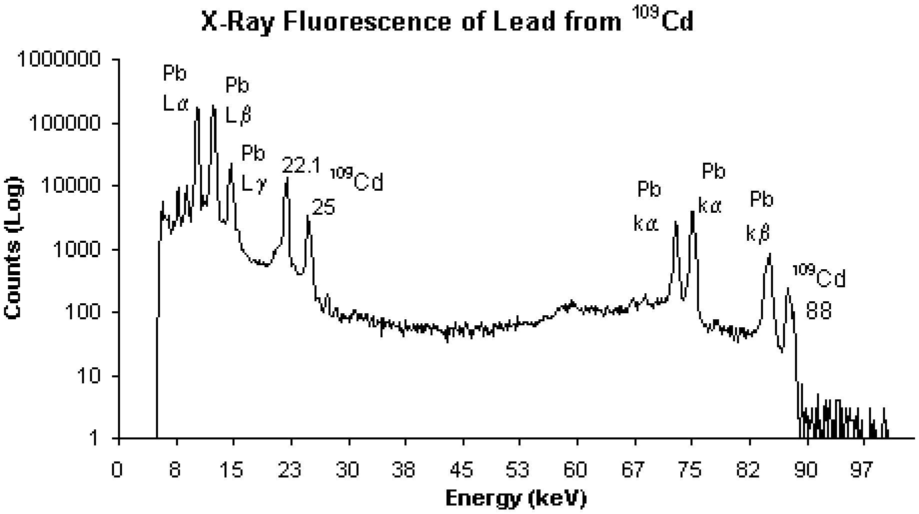

Fig. 2. X-ray energy spectrum of Pb.

X-ray fluorescence technology (XRF) provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials. It is non-destructive and reliable, requires no, or very little, sample preparation and is suitable for solid, liquid and powdered samples. It can be used for determination of a wide range of elements, from potassium (19) to uranium (92), and provides detection limits at the ppm level; it can also measure concentrations of up to 100% easily and simultaneously.

Heavy and toxic elements determination in environmental samples (geological and ecological, plants, herbs, soil, etc.) using XRF. 26 elements like K, Ca, Ti, Cr, V, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Sn, Sb, Cs, Ba, La, Pb can be determinate simultaneously in the sample. Detection limits for the different elements are between 1 and 5 mg/g depending on the matrix and Z of the element. Relative errors between 1 and 10% are typical for trace element analysis. A certain advantage of the method is the relatively simple sample preparation procedure.

Traditionally, all XRF spectrometers have been based on radioisotope excitation. However, recent advances now enable small X-ray tubes to generate X-rays in XRF spectrometers without the need for radioactive materials.

X-Ray Fluorescence analysis of the soil samples will be carried out by the X-ray fluorescent spectrometer at FLNR, JINR

Sources of the characteristic X-ray

The characteristic X-ray of the elements will be excited by ring-shaped Cd-109 (E_γ = 22.16 keV, $T_{1/2}$ = 453 days) or Am-241 (E_γ = 59.6 keV, $T_{1/2}$ = 432.2 years) sources.

XRF detector

The samples will be analyzed by X-ray fluorescence spectrometer a with Si(Li) detector (area 30 mm^2 surface, 3 mm thickness, Be window thickness 25 um, energy resolution (FWHM) – 145 eV at 5.9 keV energy).

Relating intensities to concentration

Many factors are included in this computation, which converts the measured characteristic line intensities of the elements into weight percent concentrations.

The first factor is the intensity and energy of the X-ray excitation. A second factor is, naturally, the concentration of the elements in the sample.

The final factors are the two basic physical processes going on as the X-ray energy beam interacts with the matter of the sample: **Emission and Absorption**.

Emission of X-rays from the sample depends on several things. For example, the intensity of the K_α line depends on:

* The number of incoming X-rays that will eject an electron from the K-shell. This depends on the atomic (or photoelectric) cross section for ionization, defined as the probability that the incident beam can ionize an atom and be absorbed

* The number of the characteristic X-rays thus produced that will leave the atom without being absorbed by the atom itself. This is called the fluorescent yield.

The absorption of X-rays involves both those from the incoming beam and those of the fluorescent (exiting) beam. Atoms of the sample absorb some fraction of the incoming radiation. Other atoms of the sample absorb some of the fluorescent radiation before it can reach the detector. This absorption depends on a property of the atoms of a sample called "mass absorption coefficient." These have also been carefully measured and tabulated.

Increase of quantity of analyzed substance rises up count rate until the layer gets saturated. Due to the fact that for different energies saturation layer differs and varies within wide range, when performing multielemental analysis by the means of saturated layer technique the layer of saturation is defined by estimating complete absorption of the highest energy defined or complete absorption of the primary radiation (22.16 keV for Cd-109).

There are several ways to eliminate or estimate the influence of chemical composition and adsorption characteristics of samples on the results of analysis:

1) Use thin layers for analysis.
2) Use saturated layers considering matrix influence on the flow ratio of incoherent and coherent dissipated radiation.

In case of insufficient amount of sample substance one need to perform measurements in unsaturated (intermediate) layers. In that case it is necessary to take into account dependences of analytical lines intensities of different elements on the degree of saturation of a sample.

Samples of different composition will be presented to students for elemental analysis. Content of certain heavy and toxic elements, such as Pb, Cu, Cd etc., will be determined by the analysis software WinAxil and WinFund from Canberra. This work has practical importance for ecology.

Performing the task students will get acquainted with the basics of XRF analysis, learn about preparing samples for the analysis and XRF-spectrometer measurements as well as determination of the qualitative composition of a sample and calculation of the concentrations of the given elements considering matrix effects of a sample.

The task may be done individually or within a group of 2 or 3 persons.

Project supervisor is the senior engineer of the Center of Applied Physics FLNR **Gustova M.V.** (scientific interests are radiochemistry and XRF analysis).

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