X-Ray Fluorescence (XRF): Understanding Characteristic X-Rays

What is XRF?

X-Ray Fluorescence is defined as "The emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis."

How does XRF work?

When high energy photons (x-rays or gamma-rays) are absorbed by atoms, inner shell electrons are ejected from the atom, becoming "photoelectrons". This leaves the atom in an excited state, with a vacancy in the inner shell. Outer shell electrons then fall into the vacancy, emitting photons with energy equal to the energy difference between the two states. Since each element has a unique set of energy levels, each element emits a pattern of X-rays characteristic of the element, termed "characteristic X-rays".   The intensity of the X-rays increases with the concentration of the corresponding element.

The same underlying physics produces the optical emission spectra which are often observed in high school or college labs and used in quantitative analysis. Some typical optical spectra are shown below. The inner shells of heavier elements involve higher binding energies so produce photons in the X-ray wavelength range.
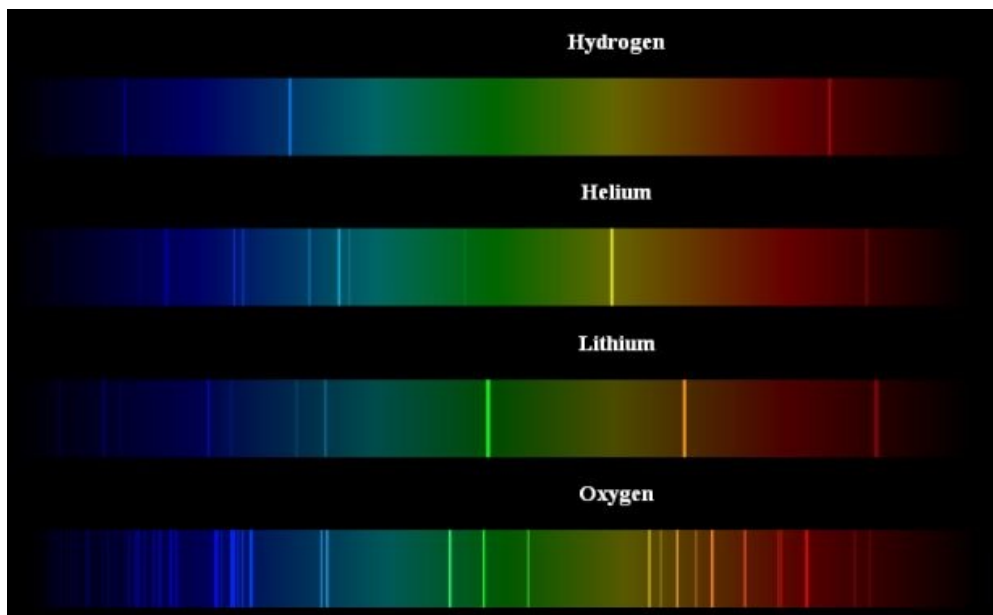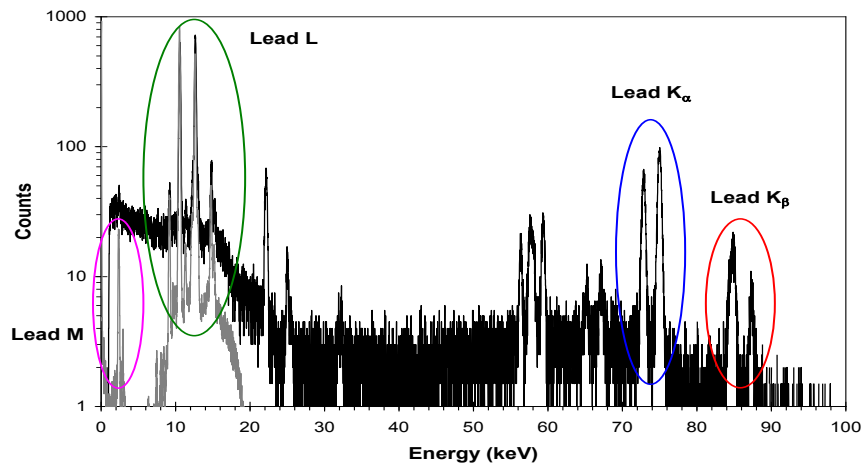
Understanding Characteristic X-Rays

   Characteristic X-rays are emitted from elements when their electrons make transitions between the atomic energy levels. If an electron transitions from a level with energy E_i to one with energy E_j, the emitted X-ray has energy $E_X=E_i-E_j$. Because each element has a unique set of atomic energy levels, it emits a unique set of X-rays which are characteristic of this element.
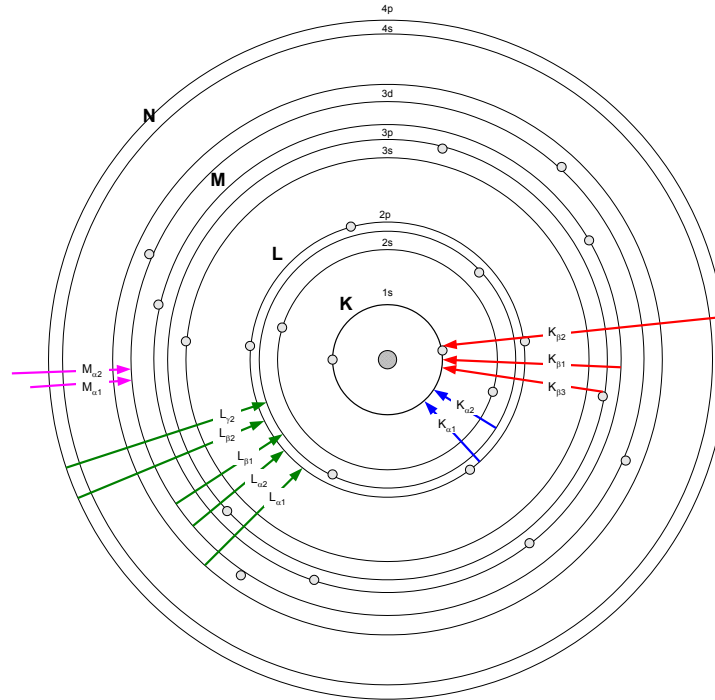
The plot above is a sketch of an atom, showing the various atomic levels, designated K, L, M, N, … Each of these has additional subshells. The characteristic X-rays arise from transitions between these shell. The plot shows how the lines are named: A K X-ray arises from a transition to the K shell from an outer shell, and so on. A $K_{\alpha 1}$ X-ray, for example, arises when there is a vacancy in the K-shell and an electron drops from the M_3 shell to fill it. The atom then emits an X-ray with energy correspond to the difference: $E_{Xray}=E_K-E_{M3}$.

This plot shows measured characteristic X-rays emitted by lead. The K shell electrons have a binding energy of 88.04 keV. The K_β lines correspond to transitions from the M and N shells, with energies of 85 and 87 keV. The K_α lines arise from transitions from the L shells, with energies of 72 and 75 keV. The L lines arise
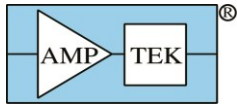
from transitions to the L shell, with energies of 10 to 15 keV. The M lines, arise from transitions to the outer M shells and have energies around 2.5 keV.
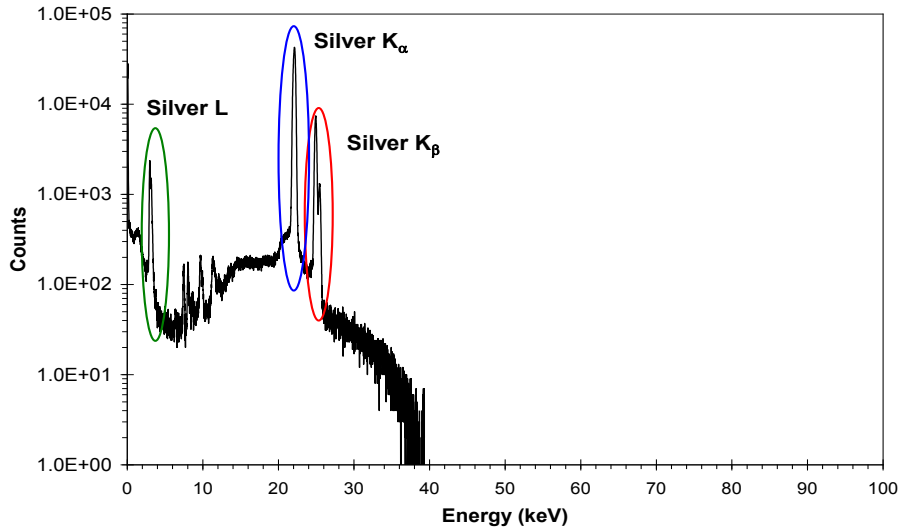

The plot above is similar, but was measured using silver. Silver, with its lower atomic number, has a binding energy of only 25.5 keV for the K shell. The X-rays are emitted at much lower energies. The plot below shows the same data, but on an expanded scale. Note that the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines, which were distinct for Pb, are not resolvable for Ag. The separation between these peaks arises from subshell splitting, i.e. spin-orbit coupling, which is much more significant for the heavier atoms.
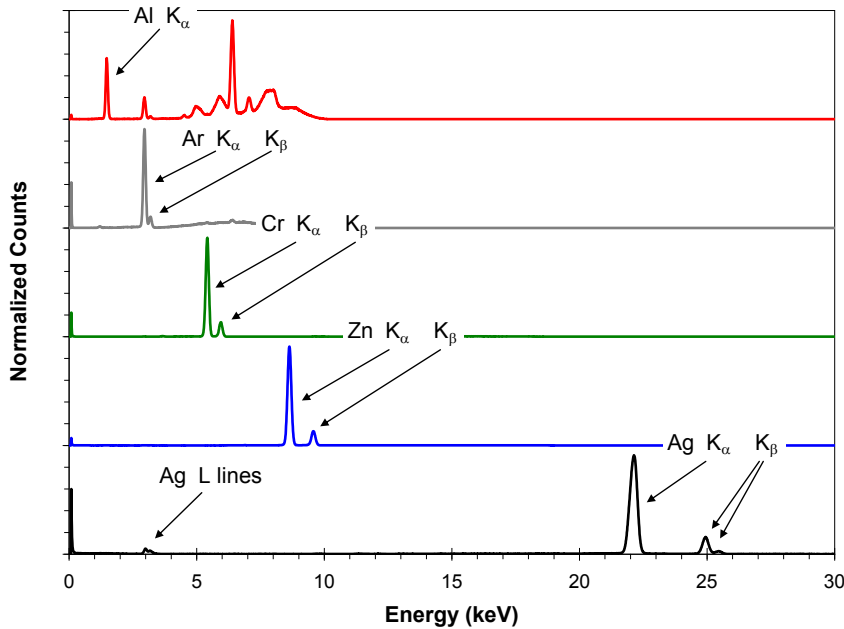

This plot shows the K lines for several elements. Each element has a clearly distinguishable signature. All the spectra shown here were measured using an XR100-SDD, with an Amptek Mini-X X-ray tube as the excitation source.

The energies of the characteristic X-ray lines depend only on the atomic energy levels so are always the same. The measured intensity of an emission lines depends on the number of corresponding atoms in the sample which were excited but on many other parameters as well. The probability of X-ray emission depends on the element and on the energy of the excitation source. The probability of detecting the X-rays depends on the detector sensitivity, attenuation in the sample itself, etc.
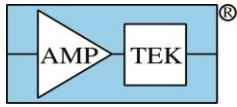
Sample XRF Spectra: Brass

The plots below show how characteristic X-ray spectra are used to determine the elements which are present in a sample. The top plot shows three spectra. One was obtained from a pure Cu sample, one from pure Zn, and one from pure Pb. Each produces a simple spectrum. Both Cu and Zn show a dominant K_α peak and then a smaller K_β peak. The Pb spectrum is more complex, dominated by two L lines, with other smaller L lines also visible.
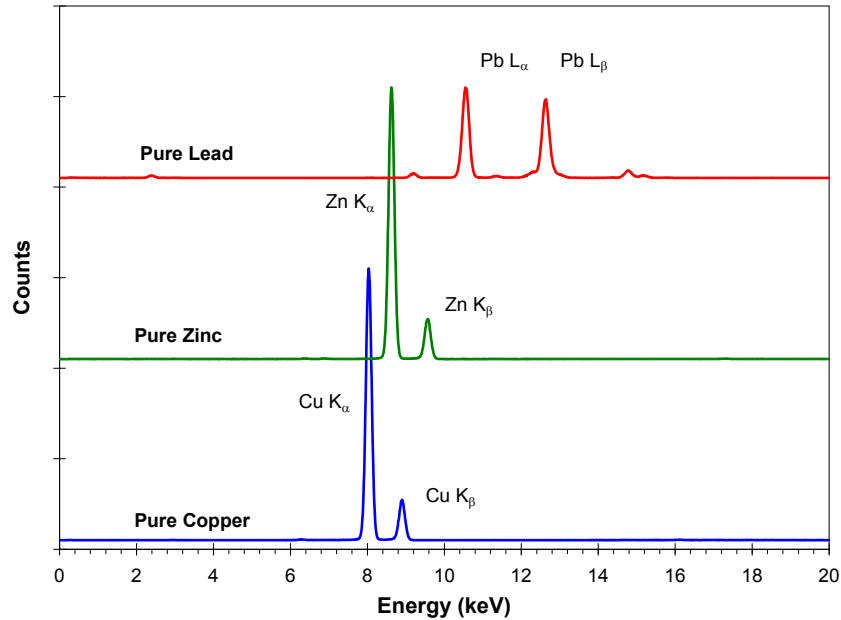
The plot below compares the three pure element spectra and a spectrum taken from a brass sample. Brass is a Cu-Zn alloy, often containing small quantities of Pb and other elements. The Cu and Zn lines are very clearly visible, with weak Pb lines. The presence of these lines indicates the presence of these elements.
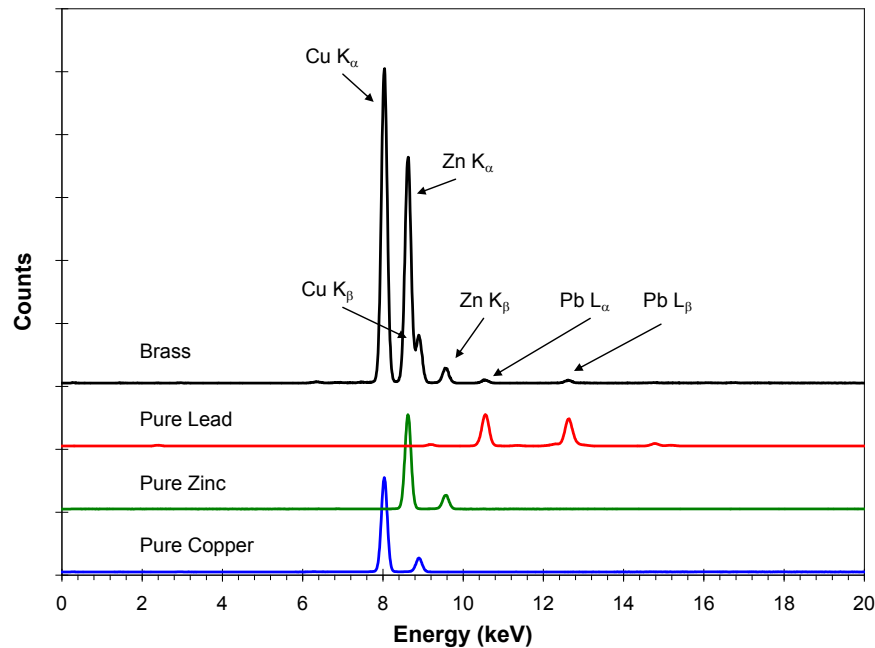
The plot below shows the same data, but the brass spectrum is shown on a logarithmic scale, which is commonly used. The linear plot above clearly shows the dominant elements. The logarithmic plot reveals
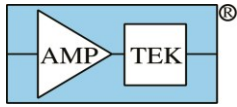
small peaks and other spectra features not seen in the linear plot. Note how some of the peaks overlap and how they lay on top of background.
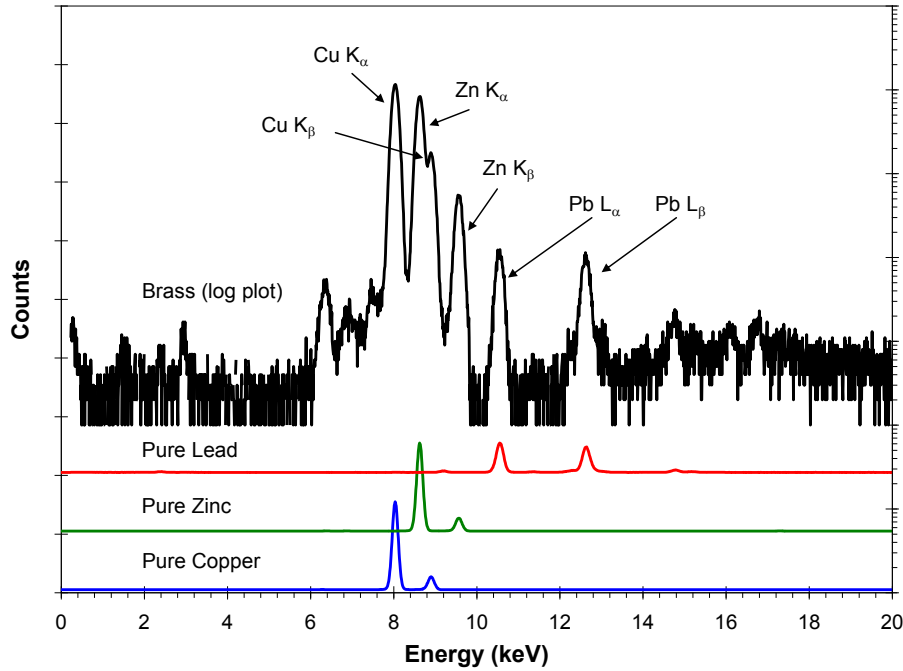
Quantitative X-ray Fluorescence

The intensities of the characteristic X-ray lines are related to the concentration of the element in the sample, but the relationship is not simple. The measured intensity of a single emission line, say the Cu K_α peak above, depends on the energy spectrum and the intensity of the exciting X-rays, on the efficiency of the X-ray detector, and on the geometry of the source and sample. It also depends on the other elements in the sample: some of the Zn K_α X-rays interact with Cu atoms in the brass sample, enhancing the Cu lines while reducing the Zn lines. These are known as matrix effects.
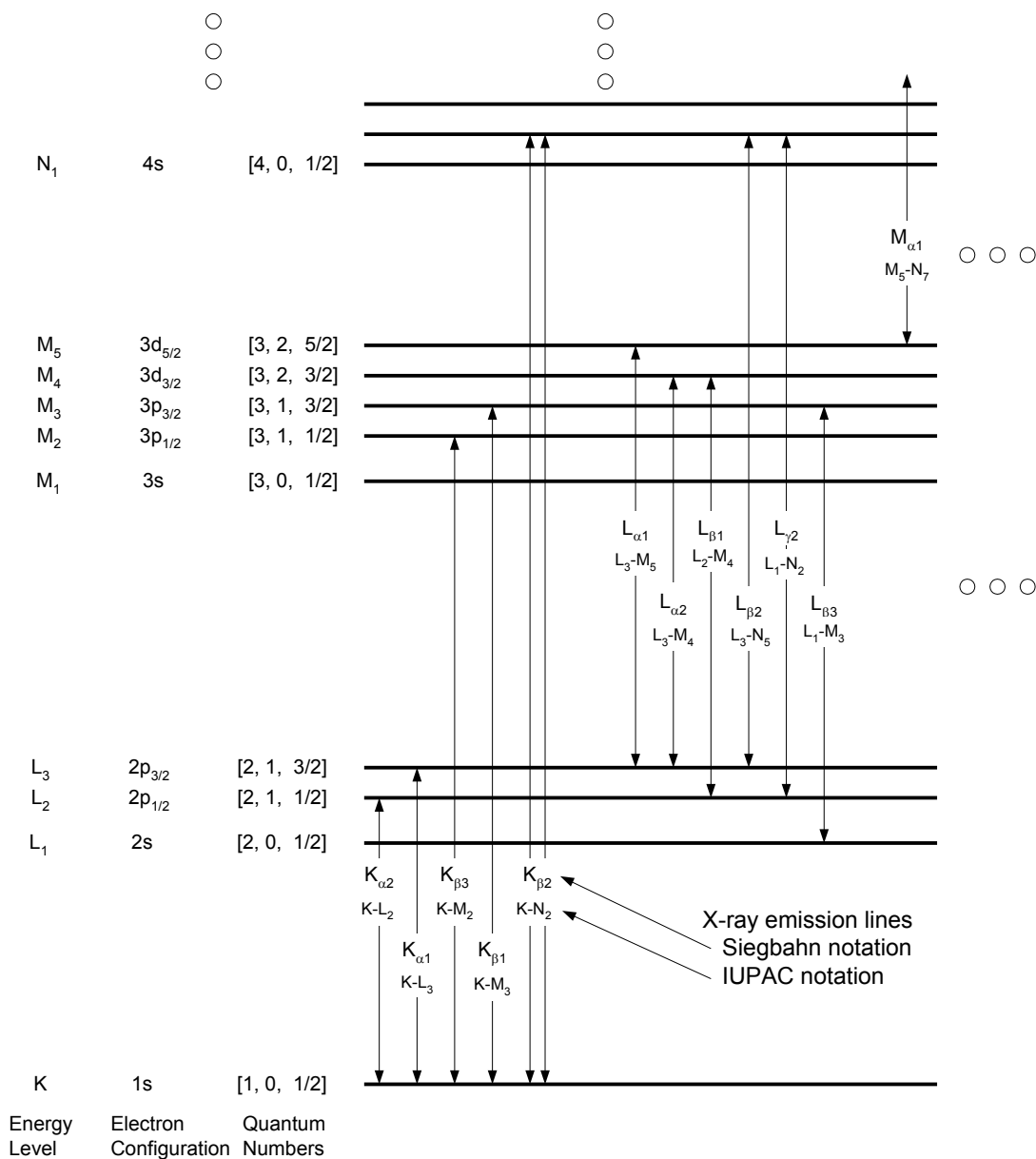
Quantitative analysis software, such as Amptek's XRS-FP, can address these complexities. There are three main steps in analyzing the spectrum. First, one must determine the intensity of each peak, i.e. the total counts, also known as net area in each peak. This requires separating the peaks from the background, correcting for escape peaks and other loss processes, and separating overlapping peaks. Second, one must correct for the sensivity of the detector and its window, for geometric effects, and for the excitation spectrum. Third, one must correct for the matrix effects.

Simple analyses may not require the full analysis software. For example, if one were interested only in the concentration of leak in the brass sample above, the concentration of Cu and Zn were nearly fixed, and the Pb concentration did not vary too much, then one could use a few calibration samples and obtain an empirical relation between net intensity of a lead peak and concentration. But for less constrained measurement conditions, more complicated analyses are necessary.
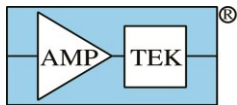
NOMENCLATURE FOR CHARACTERISTIC X-RAYS

The characteristic X-rays measured in X-ray fluorescence arise from transitions between the atomic energy levels. The name of each X-ray line corresponds to the upper and lower energy levels. The chart below illustrates the nomenclature. It is somewhat confusing, because three distinct naming systems are used for the atomic shells. Some authors refer to the energy levels (K, L_1, L_2, M_1), some to the electron configuration (1s, $2p_{3/2}$), and some to the quantum numbers [2,0,½]. The X-ray lines themselves were traditionally named using the "Siegbahn notation", developed years ago by Manne Siegbahn. The IUPAC (International Union of Pure and Applied Chemistry) recommends a different notation, which is much more rational but is not yet in common use.

Energy Level	Electron Configuration	Quantum Numbers
N_1	4s	[4, 0, 1/2]
M_5	$3d_{5/2}$	[3, 2, 5/2]
M_4	$3d_{3/2}$	[3, 2, 3/2]
M_3	$3p_{3/2}$	[3, 1, 3/2]
M_2	$3p_{1/2}$	[3, 1, 1/2]
M_1	3s	[3, 0, 1/2]
L_3	$2p_{3/2}$	[2, 1, 3/2]
L_2	$2p_{1/2}$	[2, 1, 1/2]
L_1	2s	[2, 0, 1/2]
K	1s	[1, 0, 1/2]

$M_{\alpha1}$: M_5-N_7

$L_{\alpha1}$: L_3-M_5 | $L_{\beta1}$: L_2-M_4 | $L_{\gamma2}$: L_1-N_2

$L_{\alpha2}$: L_3-M_4 | $L_{\beta2}$: L_3-N_5 | $L_{\beta3}$: L_1-M_3

$K_{\alpha2}$: K-L_2 | $K_{\beta3}$: K-M_2 | $K_{\beta2}$: K-N_2

$K_{\alpha1}$: K-L_3 | $K_{\beta1}$: K-M_3

X-ray emission lines
Siegbahn notation
IUPAC notation

The energies of the characteristic X-rays can be found in many different references. An excellent reference is available online, at http://xdb.lbl.gov/Section1/Periodic_Table/X-ray_Elements.html. This is the online version of the X-ray data booklet, from the Lawrence Berkely National Laboratory.