

4.5: X-ray Photoelectron (XPS) Spectroscopy

X-Ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is one of the most widely used surface techniques in materials science and chemistry. It allows the determination of atomic composition of the sample in a non-destructive manner, as well as other chemical information, such as binding constants, oxidation states and speciation. The sample under study is subjected to irradiation by a high energy X-ray source. The X-rays penetrate only 5 – 20 Å into the sample, allowing for surface specific, rather than bulk chemical, analysis.

Figure 4.5.1 Excitation of an electron from an atom's K-shell.

As an atom absorbs the X-rays, the energy of the X-ray will cause a K-shell electron to be ejected, as illustrated by Figure 4.5.1. The K-shell is the lowest energy shell of the atom. The ejected electron has a kinetic energy (KE) that is related to the energy of the incident beam ($h\nu$), the electron binding energy (BE), and the work function of the spectrometer (ϕ) (4.5.1). Thus, the binding energy of the electron can be calculated.

$$BE = h\nu - KE - \psi_s \quad (4.5.1)$$

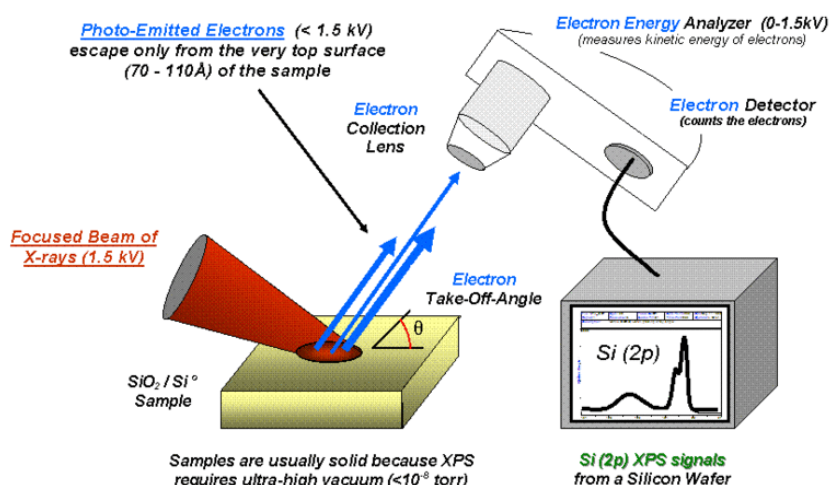


Figure 4.5.1: XPS Instrument. (Public Domain; Bvcris via Wikipedia)

Table 4.5.1 shows the binding energy of the ejected electron, and the orbital from which the electron is ejected, which is characteristic of each element. The number of electrons detected with a specific binding energy is proportional to the number of corresponding atoms in the sample. This then provides the percent of each atom in the sample.

Table 4.5.1: Binding energies for select elements in their elemental forms.

Element	Binding Energy (eV)
Carbon (C) (1s)	284.5 - 285.1
Nitrogen (N) (1s)	396.1 - 400.5
Oxygen (O) (1s)	526.2 - 533.5
Silicon (Si) (2p)	98.8 - 99.5
Sulfur (S) (2p _{3/2})	164.0 - 164.3
Iron (Fe) (2p _{3/2})	706.8 - 707.2
Gold (Au) (4f _{7/2})	83.8 - 84.2

The chemical environment and oxidation state of the atom can be determined through the shifts of the peaks within the range expected (Table 4.5.2). If the electrons are shielded then it is easier, or requires less energy, to remove them from the atom, i.e., the binding energy is low. The corresponding peaks will shift to a lower energy in the expected range. If the core electrons are not

shielded as much, such as the atom being in a high oxidation state, then just the opposite occurs. Similar effects occur with electronegative or electropositive elements in the chemical environment of the atom in question. By synthesizing compounds with known structures, patterns can be formed by using XPS and structures of unknown compounds can be determined.

Table 4.5.2 Binding energies of electrons in various compounds.

Compound	Binding Energy (eV)
COH (C 1s)	286.01 - 286.8
CHF (C 1s)	287.5 - 290.2
Nitride (N 1s)	396.2 - 398.3
Fe ₂ O ₃ (from O, 1s)	529.5 - 530.2
Fe ₂ O ₃ (from Fe, 2p _{3/2})	710.7 - 710.9
FeO (from Fe 2p _{3/2})	709.1 - 709.5
SiO ₂ (from O, 2s)	532.5 - 533.3
SiO ₂ (from Si, 2p)	103.2 - 103.9

Sample preparation is important for XPS. Although the technique was originally developed for use with thin, flat films, XPS can be used with powders. In order to use XPS with powders, a different method of sample preparation is required. One of the more common methods is to press the powder into a high purity indium foil. A different approach is to dissolve the powder in a quickly evaporating solvent, if possible, which can then be drop-casted onto a substrate. Using sticky carbon tape to adhere the powder to a disc or pressing the sample into a tablet are an option as well. Each of these sample preparations are designed to make the powder compact, as powder not attached to the substrate will contaminate the vacuum chamber. The sample also needs to be completely dry. If it is not, solvent present in the sample can destroy the necessary high vacuum and contaminate the machine, affecting the data of the current and future samples.

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