X-Ray Photoelectron Spectroscopy(XPS)

Introduction

X-ray Photoelectron Spectroscopy (XPS) emerged in the 1960s through the pioneering work of Kai Siegbahn and his team at the University of Uppsala, Sweden. Originally called ESCA (Electron Spectroscopy for Chemical Analysis), Siegbahn's contributions in this field earned him the Nobel Prize in Physics in 1981. XPS involves exposing a material to X-ray beams to analyze its electron population spectra. By examining the kinetic energy and quantity of emitted electrons, researchers can deduce the chemical composition of the sample. Operating XPS necessitates high or ultra-high vacuum conditions, although recent advancements have led to the development of ambient-pressure XPS for analysis under slightly higher pressures.

XPS finds broad application across diverse fields, including the analysis of inorganic compounds, metal alloys, polymers, catalysts, and biological materials. It entails irradiating a solid with mono-energetic X-rays in a vacuum and measuring the energy of emitted electrons to examine the surface. Plotting the number of electrons against their kinetic energy yields a spectrum, with each element showing a unique range. By summing the peaks of individual components, researchers can estimate the spectrum of a mixture of elements. XPS is particularly valuable for surface analysis, as it detects electrons from only the top few atomic layers due to the minimal mean free path of electrons in solids. Peak heights and areas provide quantitative data, while peak positions, separations, and other spectral properties aid in identifying chemical states.
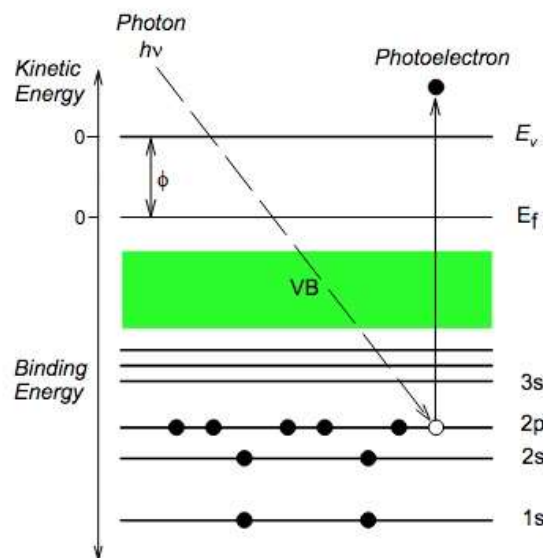
Basic Principle

Surface analysis using XPS involves irradiating a sample with mono-energetic, soft X-rays and examining the energy of the emitted electrons. Typically, Mg Kα (1253.6 eV) or Al Kα (1486.6 eV) X-rays are employed for this purpose. These photons have restricted penetrating power, reaching depths in

the solid on the order of 1-10 micrometers. Upon interaction with atoms at the surface, they induce the emission of electrons via the photoelectric effect. The kinetic energy of the emitted electrons is given by the formula:

$$KE = h\upsilon - (BE - \phi_s)$$

where $h\upsilon$ is the energy of the photon, BE is the binding energy of the atomic orbital from which the electron originates, and ϕ_s is the spectrometer work function.

Photon
$h\nu$

Photoelectron

Kinetic Energy

0 — E_v

ϕ

0 — E_f

VB

Binding Energy

3s

2p

2s

1s

The energy difference between the initial and final states after the photoelectron leaves the atom is known as the binding energy. Because ions of all atom types can have a large number of possible terminal states, the electrons that are released can have a wide variety of kinetic energies. Additionally, every end state has a distinct probability or cross-section. The concentration of the elements present on the surface can be identified and ascertained using XPS since every element has a distinct set of binding energies. Disparities in the compounds' polarizability and chemical potential result in variations in the elemental binding energies, or the chemical shifts. The chemical state of the materials under study can be ascertained using these alterations in composition. Apart from the

photoelectrons released during the photoelectric process, the relaxation of the excited ions that remain after photoemission can also release Auger electrons.
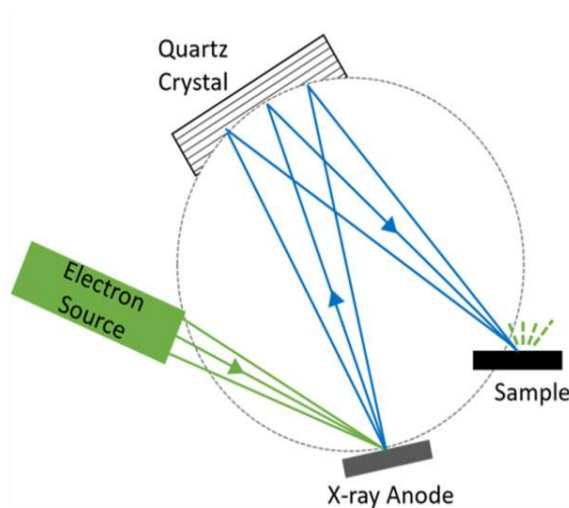
After the photoelectric process, Auger electron emission typically occurs within 10 to 14 seconds. In this Auger process, an outer electron fills an inner orbital vacancy while simultaneously emitting a second electron to dissipate excess energy. Despite the initial ionization mode, the Auger electron's kinetic energy equals the difference between the original ion's energy and the final doubly charged ion's energy. Hence, during photoionization, both an Auger electron and a photoelectron are usually emitted. However, the total kinetic energy of these electrons is not enough to surpass the energy of the ionizing photons.

While photons travel in micrometer-scale paths, electrons move in paths measured in tens of angstroms due to their higher interaction with matter. Thus, only electrons originating within tens of angstroms below the solid surface can escape without losing energy, despite ionization reaching depths of a few micrometers. These electrons are crucial as they depart the surface without energy loss, creating peaks in spectra. An electron spectrometer uses their kinetic energy to identify departing electrons from the sample. Typically, the analyzer acts as a pass energy window, only accepting electrons with energies within the window's range. The pass energy remains constant, and incoming electrons are adjusted to this energy before entering the analyzer to maintain consistent energy resolution.

To facilitate scanning for various energies, a variable electrostatic field is applied in front of the analyzer. This retardation voltage can be adjusted from zero to the photon energy and beyond. During the data recording process, the number of electrons for a specific detection time and energy is captured, with electrons being detected as discrete occurrences.

Instrumentation

The XPS equipment is contained within an ultra-high vacuum environment, encompassing components such as an X-ray source, sample stage, extraction lenses, analyzer, and detector. Below is a schematic diagram illustrating an XPS system:

XPS instruments are housed in ultra-high vacuum (UHV) environments for two main purposes. Firstly, to inhibit emitted electrons from scattering off air molecules during their journey to the analyzer, necessitating vacuum levels typically between 10^{-5} to 10^{-6} mbar. In practice, XPS systems generally operate at significantly lower base pressures, typically in the range of 10^{-9} to 10^{-10} mbar. Given its surface sensitivity, XPS is highly susceptible to surface contamination. For instance, at a pressure of 1×10^{-6} mbar and a sticking coefficient of 1 (meaning every molecule striking the surface adheres to it), contamination would accumulate at a rate of one monolayer every 2 seconds. Therefore, XPS instruments utilize ultra-high vacuum (UHV) environments to minimize surface contamination within the chamber.

Various parts of an XPS instrument are explained below:

A. X-ray sources: Electrons from these sources are accelerated towards a high-voltage anode by means of a heated filament made of tungsten or lanthanum hexaboride (LaB_6). The selection of the anode material is dependent upon multiple factors:

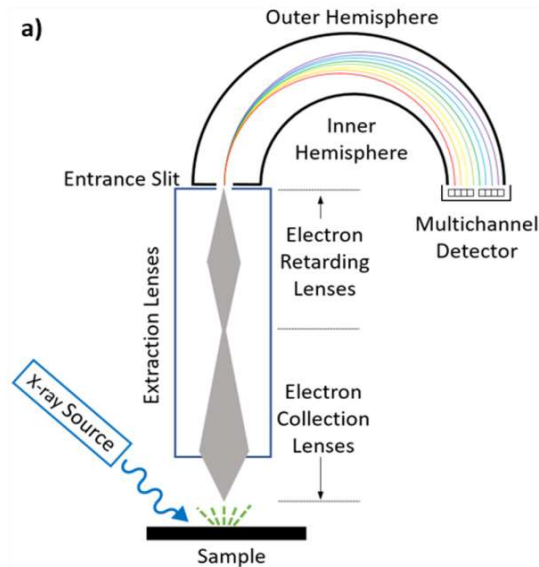1) Energy: Measurable transitions are determined by the source's energy.

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B. The lenses, analyzer, and detector: Between the sample and the analyzer in an XPS system, there are electron optics known as extraction lenses, which serve various functions. These lenses determine the acceptance angle for collecting electrons emitted from the sample. Typically, a larger acceptance angle enhances the efficiency of electron collection. The energy resolution in XPS is constrained by the energy of the detected electrons; higher energy electrons lead to lower resolution. Therefore, the extraction lenses often adjust or retard the energy of the electrons to a specific user-defined value, known as the pass energy, before they enter the analyzer. This adjustment helps achieve the desired energy resolution in the analysis. Resolution and electron throughput are impacted by the pass energy. Smaller pass energies are usually employed for high-resolution scans because they yield superior spectral resolution with fewer electrons identified. Higher pass energies, on the other hand, are utilized for survey scans since they can provide more electron throughput in situations where resolution is not crucial. For XPS systems, two primary types of analyzers were created: concentric hemispherical analyzers and cylindrical mirror analyzers. All commercial XPS

systems today employ the concentric hemispherical analyzer architecture, which over time shown to have superior performance in terms of energy resolution and eventually throughput. The concentric

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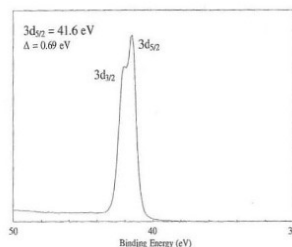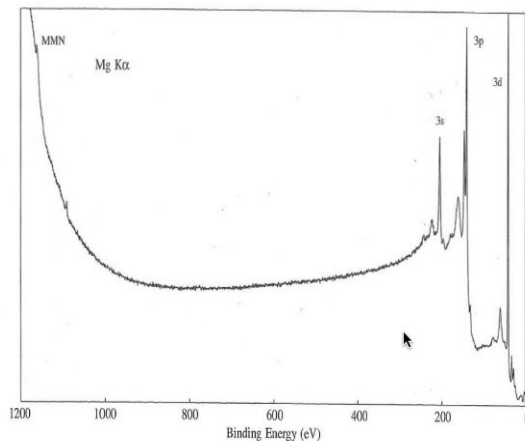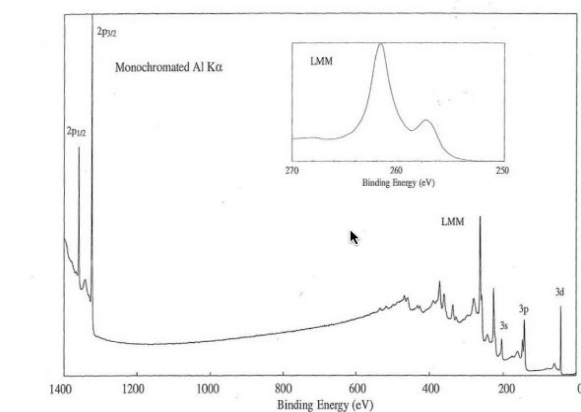
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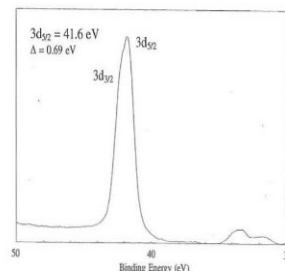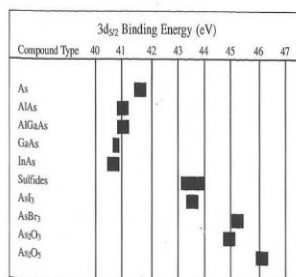
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In order to identify the elements present in the sample and determine peak shapes and chemical shifts, a typical XPS data collecting strategy entails first obtaining high-resolution spectra of the components of interest. Depending on the number of high-resolution scans required and the element concentrations in the sample, data gathering typically takes 30 to 60 minutes per sample.
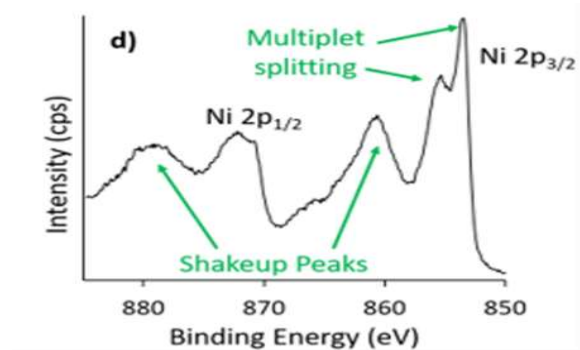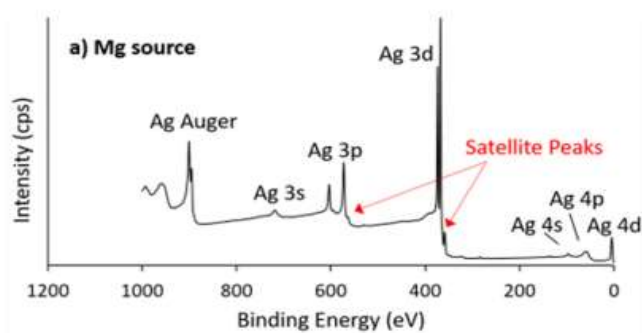
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Several decisions need to be made by the researcher during preparation for data acquisition, including the selection of the X-ray source, setting scan parameters, determining which lines to analyze, and deciding whether to employ charge neutralization.

- X-ray Source: The depth of analysis, spectral resolution, and observable transitions are all impacted by the X-ray source selection. Although there are theoretically many different X-ray sources, researchers are usually restricted to the sources that are available on the XPS system they are using, with Mg and Al being the most widely available sources.

- Scan Parameters: To guarantee high-quality data gathering, parameters including pass energy, step size, and dwell time must be properly configured. These parameters are user-controlled. These parameters varies between equipment and for survey and high-resolution spectra. Survey spectra, which usually use bigger pass energies and longer steps with relatively short dwell durations, demand high electron throughput but place less emphasis on spectral precision.

- **High-Resolution Lines to Scan:** Selecting lines for high-resolution analysis is a decision that researchers must make. The greatest intensity peak for a particular element is often selected based on how simple it is to detect and how readily reference data is available.

- **Neutralization of Charge:** During XPS examination, insulating samples may charge, resulting in undesired peak shifts and distortions. Charge neutralizers are vacuum chamber components that are positioned above the sample and serve as a source of low-energy electrons or ions to counteract charging effects. They are especially useful for insulating samples.

- **Peak Identification:** Based on energy levels and transitions, each element has a distinct XPS spectrum that helps with identification. For peak identification, reference books with spectra of each element are advised. These books offer details on peak energy, chemical changes, anticipated peak splitting, and forms. Libraries of peak positions are also provided by software analysis packages; however, reference books are still a good source of supplementary information about things like chemical changes and peak shapes.

There are some more types of peaks that do appear in spectra usually that can create some confusion for new XPS users.

Satellite peaks, as seen in the above picture, arise from the excitation of a material with multiple x-ray energies, producing additional XPS peaks with lower binding energies. One can eliminate these satellite peaks by using a monochromatic X-ray source. Shakeup peaks, often referred to as loss

peaks, are the product of a process known as de-excitation, in which a valence electron is excited to a higher energy level through interaction with the outgoing core electron.

Data Analysis and Interpretation

Quantitative analysis: The capability of XPS to calculate atomic concentrations without the need for standards is a crucial feature. The area beneath a peak can be measured after subtracting the baseline, but raw areas cannot be utilized to calculate relative concentrations on their own. Rather, each transition requires a unique sensitivity factor, as given by the equation.

$$C_x = (I_x/S_x)/(\Sigma(I_i/S_i))$$

x is the species of interest, i stands for all potential species, S for sensitivity factor, C for atomic concentration, and x is the peak area or intensity. A transition with a higher sensitivity factor is expected to have a stronger signal and be simpler to perceive than one with a lower sensitivity factor. Sensitivity factors for a few often examined items are displayed in the table below:

Element	Sensitivity factor	Element	Sensitivity factor	Element	Sensitivity factor
C 1s	1.00	Ca 2p	5.13	Ag 3d	18
N 1s	1.77	Cr 2p	11.5	In 3d	22.4
O 1s	2.85	Ni 2p	21.1	Sn 3d	24.7
F 1s	4.26	Ni 2p 3/2	13.9	Hf 4f	7.95
Na 1s	7.99	Ni 2p 1/2	7.18	Ta 4f	9.07
Al 2p	0.5735	Cu 2p	24.1	W 4f	10.3
Si 2p	0.865	Ga 2p	31	Pt 4f	15.9
Cl 2p	2.36	Mo 3d	9.74	Au 4f	17.4

For instance, suppose a sample spectrum indicates the presence of gold and carbon, and if the intensities of the Gold 4f and Carbon 1s peaks are equal, then there would be approximately 17.4 times more C than Au ($S_{Au\,4f}/S_{C\,1s}$ = 17.4/1).

Application Example

X-ray Photoelectron Spectroscopy (XPS) finds broad application in analyzing both naturally occurring and synthetic materials. It is utilized extensively in the examination of surface-mediated processes like sorption, catalysis, REDOX reactions, as well as dissolution and precipitation phenomena. Its applications span various fields including:

- Material Science: XPS aids in analyzing the composition and surface chemistry of materials, offering insights into their properties and behaviour.

- Polymers: XPS is used to study the surface characteristics of polymers, providing information on chemical composition, oxidation states, and bonding configurations.

- Medical Devices: XPS helps in assessing the surface properties of medical devices, ensuring their performance, biocompatibility, and durability.

- Thin Films and Coatings: XPS enables the characterization of thin films and coatings, revealing details about their composition, thickness, and interface interactions.

- Microelectronic Devices: XPS is employed in the analysis of microelectronic devices, aiding in quality control, failure analysis, and materials optimization.

- Medical and Biological Samples: XPS assists in studying the surfaces of biological and medical samples, facilitating research in areas such as biomaterials, drug delivery systems, and tissue engineering.

- Geologic Materials: XPS is utilized to investigate the surface chemistry of geological materials, helping understand processes such as weathering, mineral formation, and environmental interactions.

Limitation of the Technique

- XPS operates in a highly controlled vacuum environment, typically below 10^{-9} Torr, where some samples may become unstable or volatile.

- Unlike electron beams, X-ray beams cannot be focused tightly, resulting in a larger surface area being analyzed. Typically, the analyzed area ranges from millimeters to tens or hundreds of microns, providing an averaged signal across these regions. While modern XPS instruments offer "small spot" capabilities, achieving this requires manually reducing the beam size, leading to lower count rates. Alternatively, small spot XPS can be done using X-rays from synchrotron sources.

- While charge compensation usually works well, certain samples may cause significant charging issues that affect the quality of the analysis.

- Due to its focus on surface properties, XPS is not suitable for identifying bulk material substrates.

References

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by Haribhajan Kushwaha

Introduction

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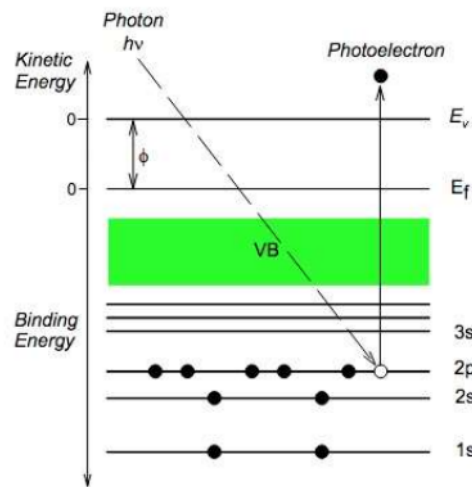
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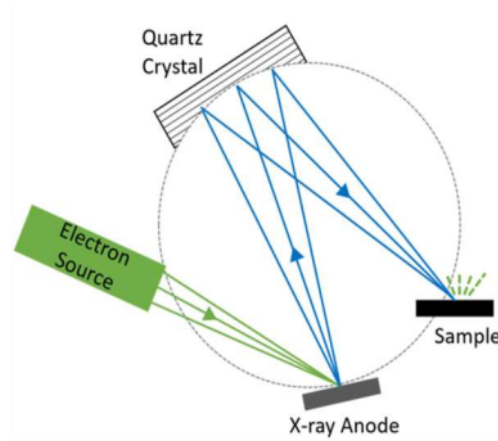
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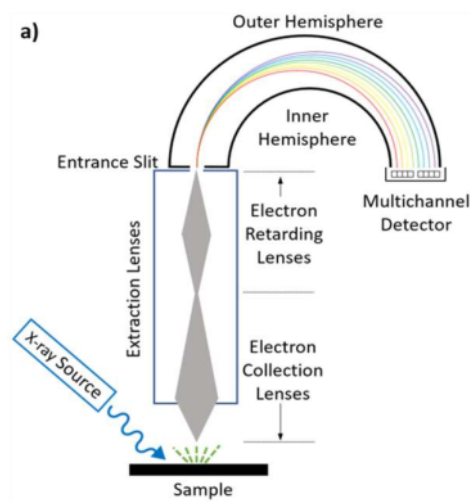1) Energy: Measurable transitions are determined by the source's energy.

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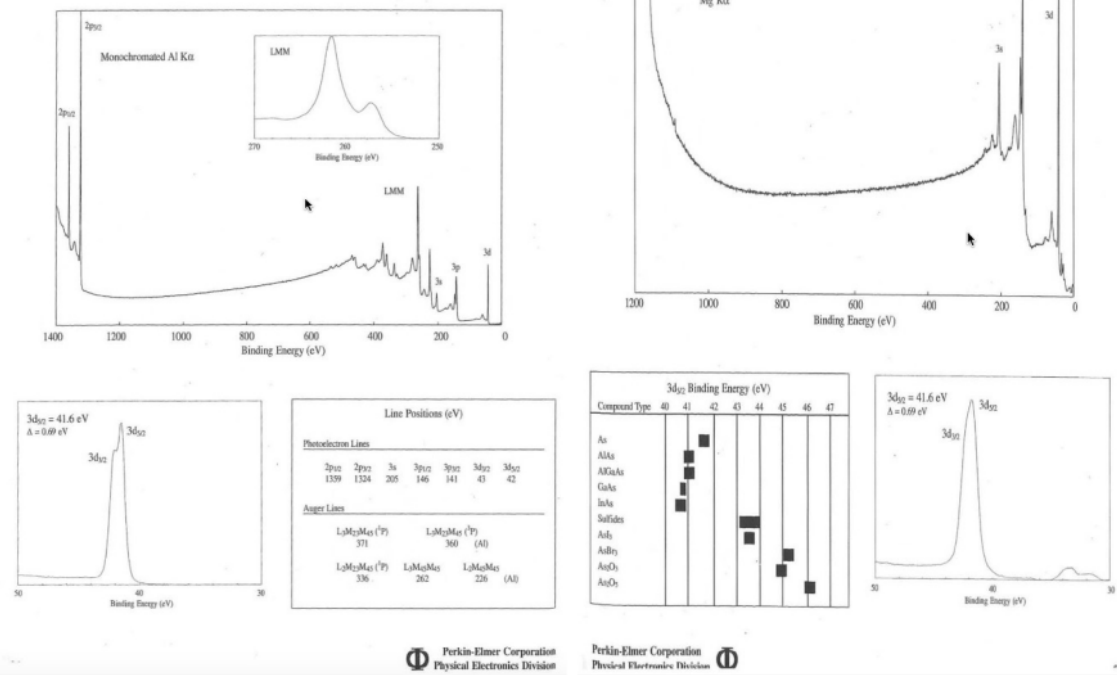
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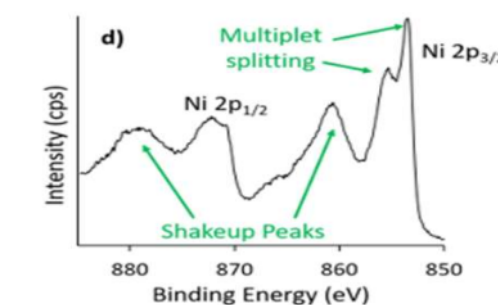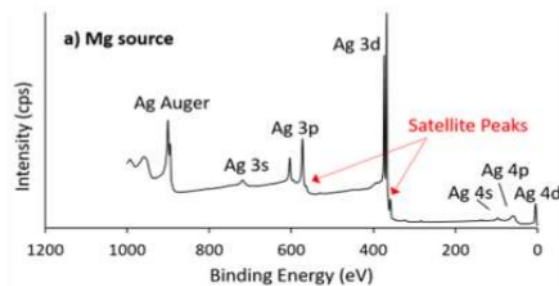
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peaks, are the product of a process known as de-excitation, in which a valence electron is excited to a higher energy level through interaction with the outgoing core electron.

Data Analysis and Interpretation

Quantitative analysis: The capability of XPS to calculate atomic concentrations without the need for standards is a crucial feature. The area beneath a peak can be measured after subtracting the baseline, but raw areas cannot be utilized to calculate relative concentrations on their own. Rather, each transition requires a unique sensitivity factor, as given by the equation.

$$C_x = (I_x/S_x)/(\Sigma(I_i/S_i))$$

x is the species of interest, i stands for all potential species, S for sensitivity factor, C for atomic concentration, and x is the peak area or intensity. A transition with a higher sensitivity factor is expected to have a stronger signal and be simpler to perceive than one with a lower sensitivity factor. Sensitivity factors for a few often examined items are displayed in the table below:

Element	Sensitivity factor	Element	Sensitivity factor	Element	Sensitivity factor
C 1s	1.00	Ca 2p	5.13	Ag 3d	18
N 1s	1.77	Cr 2p	11.5	In 3d	22.4
O 1s	2.85	Ni 2p	21.1	Sn 3d	24.7
F 1s	4.26	Ni 2p 3/2	13.9	Hf 4f	7.95
Na 1s	7.99	Ni 2p 1/2	7.18	Ta 4f	9.07
Al 2p	0.5735	Cu 2p	24.1	W 4f	10.3
Si 2p	0.865	Ga 2p	31	Pt 4f	15.9
Cl 2p	2.36	Mo 3d	9.74	Au 4f	17.4

For instance, suppose a sample spectrum indicates the presence of gold and carbon, and if the intensities of the Gold 4f and Carbon 1s peaks are equal, then there would be approximately 17.4 times more C than Au ($S_{Au\ 4f}/S_{C\ 1s} = 17.4/1$).

Application Example

X-ray Photoelectron Spectroscopy (XPS) finds broad application in analyzing both naturally occurring and synthetic materials. It is utilized extensively in the examination of surface-mediated processes like sorption, catalysis, REDOX reactions, as well as dissolution and precipitation phenomena. Its applications span various fields including:

- Material Science: XPS aids in analyzing the composition and surface chemistry of materials, offering insights into their properties and behaviour.

- Polymers: XPS is used to study the surface characteristics of polymers, providing information on chemical composition, oxidation states, and bonding configurations.

- Medical Devices: XPS helps in assessing the surface properties of medical devices, ensuring their performance, biocompatibility, and durability.

- Thin Films and Coatings: XPS enables the characterization of thin films and coatings, revealing details about their composition, thickness, and interface interactions.

- Microelectronic Devices: XPS is employed in the analysis of microelectronic devices, aiding in quality control, failure analysis, and materials optimization.

- Medical and Biological Samples: XPS assists in studying the surfaces of biological and medical samples, facilitating research in areas such as biomaterials, drug delivery systems, and tissue engineering.

- Geologic Materials: XPS is utilized to investigate the surface chemistry of geological materials, helping understand processes such as weathering, mineral formation, and environmental interactions.

Limitation of the Technique

- XPS operates in a highly controlled vacuum environment, typically below 10^{-9} Torr, where some samples may become unstable or volatile.

- Unlike electron beams, X-ray beams cannot be focused tightly, resulting in a larger surface area being analyzed. Typically, the analyzed area ranges from millimeters to tens or hundreds of microns, providing an averaged signal across these regions. While modern XPS instruments offer "small spot" capabilities, achieving this requires manually reducing the beam size, leading to lower count rates. Alternatively, small spot XPS can be done using X-rays from synchrotron sources.

- While charge compensation usually works well, certain samples may cause significant charging issues that affect the quality of the analysis.

- Due to its focus on surface properties, XPS is not suitable for identifying bulk material substrates.

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