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A PRESENTATION ON X RAY PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

X-Ray photoelectron spectroscopy is a technique which measures the elemental composition, empirical formula, chemical state and electronic state of the elements which exists within a material. It uses low energy monochromatic x rays to excite electrons from atoms near the surface of a sample. XPS systems are widely used in treatment of cancer and other chronic diseases. Iron oxide nano particles are accurately characterized and used in treatment to destroy the malignant cells. Technologically advanced XPS systems are highly preferred by researches and scientists in discovering drugs for chronic diseases such as cancer. This article includes the principle on which XPS works, brief description of origin and interaction of rays, its instrumentation, working and applications. X ray photoelectron spectroscopy is used in bioengineering to introduce targeted medicines and increasing adoption of XPS systems amongst researches and scientists. Growing use of XPS will boost industry growth.

KEYWORDS: x-ray photoelectron, ultra high vacuum, photo ejected electrons, monochromatization, photo multiplier tube.

INTRODUCTION

X ray photoelectron spectroscopy is a spectroscopic technique which measures the elemental composition, empirical formula, chemical state and electronic state of the elements exists within a material. XPS is also known as ESCA (electron spectroscopy for chemical analysis). A variety of x ray techniques and methods are in use, they are mainly classified into three main categories. These are x ray absorption, x ray diffraction method and x ray fluorescence methods.

(A). X Ray Absorption Methods

In these methods a beam of x rays is allowed to pass through the sample and the attenuation or fraction of x ray photons absorbed is considered to be a measure of the concentration of the absorbing substance. X ray absorption methods are helpful in certain cases like elemental analysis and thickness measurements.

(B). X Ray Diffraction Methods

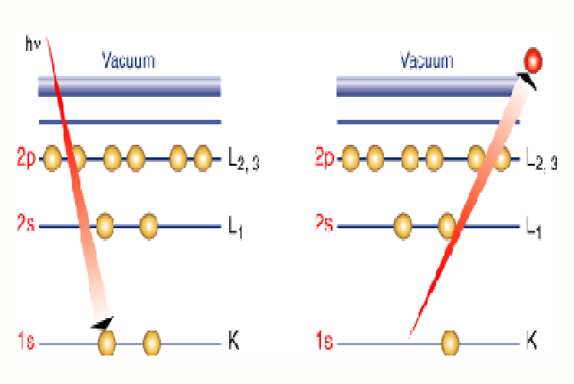
These methods are based on scattering of x rays by crystals. By these methods one can identify crystal structures of various solid compounds. These methods are extremely important as compared with x ray absorption and x ray fluorescence methods.

(C). X Ray Fluorescence Methods

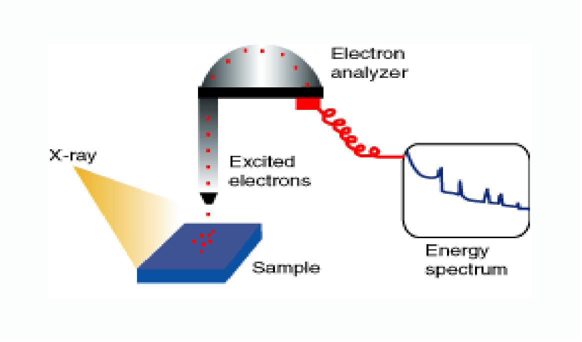
In these methods x rays are generated within the sample and by measuring wavelengths and intensity of the generated x rays one can perform qualitative and quantitative analysis. X ray fluorescence method is non-destructive and frequently requires very little sample preparation before the analysis can be carried out.

Principle

X-ray photoelectron spectroscopy (XPS) is a surface characterization technique that can analyse a sample to a depth of 2 to 5 nanometres (nm). Kai Siegbahn, who won the Nobel Prize in physics in 1981 for his research, developed XPS in the 1960s. XPS reveals which chemical elements are present at the surface and the nature of the chemical bond that exists between these elements. It can detect all of the elements except hydrogen and helium. Photoemission principle: When an x-ray (red arrow) bombards a sample (left), some electrons (yellow spheres) become excited enough to escape the atom (right). XPS is conducted in ultrahigh vacuum (UHV) conditions, around 10-9 millibar (mbar). Atmospheric pressure is about 1 bar, which means that the number of atoms of gas in a UHV chamber is one-trillionth that of air per unit of volume. The ambient atmosphere that a sample is exposed to can change its properties. For example, at a pressure of 10-6 mbar, background gas constituents (O2, H2O, etc.) can react with the surface of a sample in several seconds. Even under optimal instrumental conditions this is too little time in which to conduct an experiment. However, at UHV pressures it takes hours before a sample significantly degrades, thus enabling accurate surface interrogation using XPS.



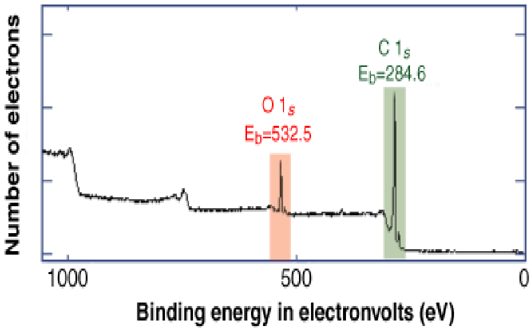
Irradiating a sample with x-rays of sufficient energy results in electrons in specific bound states to be excited. In a typical XPS experiment, sufficient energy is input to break the photoelectron away from the nuclear attraction force of an element. Two key features are derived from XPS data. The first is that even photo-ejected electrons from core levels have slight shifts depending on the outer valence configuration of the material examined. The second is that the specific energy of an elemental core level transition occurs at a specific binding energy that can uniquely identify (and in favourable cases quantify) the element. In a typical XPS spectrum some of the photo-ejected electrons inelastically scatter through the sample enroute to the surface, while others undergo prompt emission and suffer no energy loss in escaping the surface and into the surrounding vacuum. Once these photo-ejected electrons are in the vacuum, they are collected by an electron analyzer that measures their kinetic energy. An electron energy analyzer produces an energy spectrum of intensity (number of photo-ejected electrons versus time) versus binding energy (the energy the electrons had before they left the atom). Each prominent energy peak on the spectrum corresponds to a specific element. In the spectrum below, there is a peak at 284.6 electron volts (eV), which corresponds to carbon, and a peak at 532.5 eV, which corresponds to oxygen; therefore, this sample contains carbon (C) and oxygen (O).



Besides identifying elements in the specimen, the intensity of the peaks can also tell how much of each element is in the sample. Each peak area is proportional to the number of atoms present in each element. The specimen chemical composition is obtained by calculating the respective contribution of each peak area.

By applying relative sensitivity factors and appropriately integrating peak areas, it can be determined that the sample below is 25 percent oxygen and 75 percent carbon.

By studying the energy of the carbon peak, it can also be determined if the surface of this material corresponds to a C-O single bond (ethers, alcohols) or a much stronger C=O double bond (carboxylates, ketones). Core level shifts are important in determining valence states in metals, transition metal oxides, and actinide materials.



Theory

1. Origin of X Rays

The x ray region of the electromagnetic spectrum consists of wavelengths in the region of about 0.1 to 100AO. X rays are generated when high velocity electrons impinge on a metal target. The process of producing x rays may be visualised in terms of Bohr's theory of atomic structure.

An atom is composed of a nucleus and numerous electrons. The electrons are arranged in layers or shells with the valence electrons in the outer shell.

The different shells or layers of electrons are called the K shell, L shell, M shell and so on. For example a sodium atom contains filled K and L shells and one electron in the M shell.

Whenever a fast moving electron impinges on an atom, it may knock out an electron completely from one of that atom. Following the loss of inner shell electron one of the outer electrons will fall into the vacated orbital, with the simultaneous emission of an X ray photon. The energy the emitted x ray photon is equal to the difference in energy between the two levels involved. For instance, if a K shell loses its one electron, and it is replaced by the electron from the L shell, the resulting x ray is

termed as K X ray and its energy E'K is given as follows:
E'K = EL –EK.

Where EL and EK are the energies of L and K shell electrons respectively.

2. INTERACTION OF X RAY WITH MATTER:-The X rays can interact with matter in three ways absorption, scattering and diffraction.

(a) Absorption
If a beam of x ray is allowed to pass through matter, it loses energy partly by scattering and partly by true absorption. The absorption of X-rays means that the electrons of the atoms constituting the matter absorb energy from these rays and get excited. Then these excited electrons emit secondary radiations characteristic of those atoms.

However, if mass absorption coefficients are plotted against wavelength of x-rays, the curves obtained are not smooth but show a series of discontinuities known as absorption edges which occur at definite wavelengths for each element. At these wavelengths the energy of x-ray beam is sufficient to cause ejection of electrons from the lower atomic orbital and the mass absorption coefficient therefore rises sharply. It is important emphasize that the extent of absorption by a given element depends on the number of atoms of that element in the path of x-rays but it is independent of the physical or chemical state of that element. For example, the amount of absorption by a given number of Iodine atoms will remain same whether we take Iodine in the form of a diatomic gas, a liquid, or a solid.

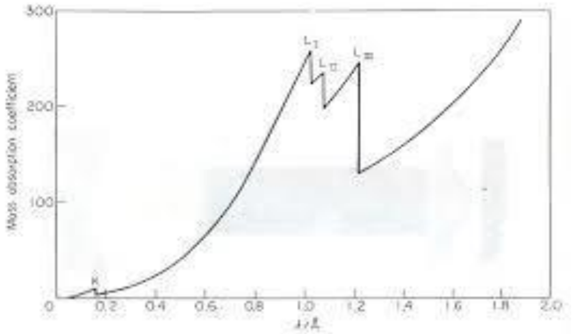
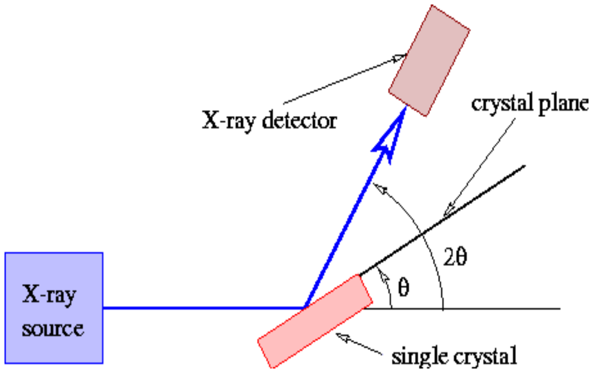


Fig. 3-2 Variation of mass absorption coefficient with wavelength

With x-ray absorption we can tell if a bone is fractured or if we have rocks in our head. By using x-ray absorption we can also measure how much liquid is in a can or a storage tank without taking the liquid of tank out or opening the container.

(B) Scattering and Diffraction: When a beam of X radiation is incident upon a substance, the electrons constituting the atoms of the substance become as small oscillators. These on oscillating at the same frequency as that of incident X-radiation, emit electromagnetic radiations in all directions at the same frequency as the incident X- radiation. These scattered waves are coming from electrons which are arranged in a regular manner in a crystal lattice and then travelling in certain directions. If these waves undergo constructive interference, they are said to be diffracted by the crystal plane. Every crystalline substance scatters the x-rays in its own unique diffraction pattern producing a fingerprint of its atomic and molecular structure. The conditions for diffraction are governed by Bragg's law and the diffracted beams are often referred to as reflections. Constructive interference of the reflected beams emerging from two different planes will take place if the difference in the path lengths of two rays is equal to whole number of wavelengths.



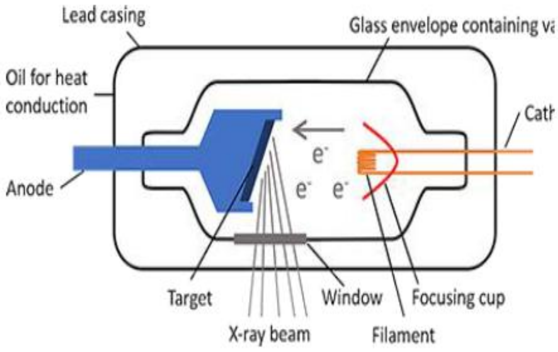
Through x-ray diffraction we can identify the crystal structures of various solid compounds and identify a compound from its structure. We can also determine the arrangement of molecules in a crystal. This has enabled us to obtain invaluable information on the structure of such diverse materials as chemical crystals, metals, and living tissue.

(C) Fluorescence
If a sample is irradiated with an x-ray beam, the sample sometimes, emits other x-ray beams this process is called x-ray fluorescence. The wavelength of x-ray fluorescence enables us to determine what element is present in a sample. The intensity of x-rays that are emitted enables us to determine how much is present. It provides us with a method of elemental analysis that is independent of molecular structure in which the element finds itself. The method is also non-destructive and frequently requires very little sample preparation before the analysis can be carried out.

Instrumentation
X-ray absorption, x-ray diffraction and x-ray fluorescence are the three main fields of x-ray spectroscopy. Only optical system varies in each case although component parts of the equipment are the same. The main components are described as follows:

(1) Production of X-Rays
X-rays are generated when high velocity electrons impinge on a metal target. Approximately, 1% of total

energy of the electron beam is converted into X-radiation, the remainder being dissipated as heat. Many types of x-ray tubes are available which are used for producing x-rays.

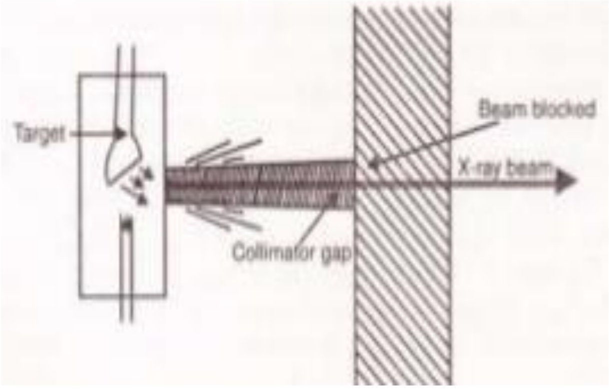


Generally, the target gets very hot in use. This problem has been solved to some extent by cooling the tube with water. Another method of solving this problem is to rotate the target at high speed so that the production of localised heating is reduced. Ne extra advantage of this method is that it permits the production of x-rays of intensity much greater than that obtainable from stationary target. One disadvantage of most x-ray tubes is that there is lack of focussing of the electron so that whole surface becomes a source of x-rays.

In one model, the small focus of electron beam has been achieved by using a spherical electrostatic lens within the electron gun of the x-ray tube. By this method electron beam smaller than one micron in diameter can be produced.

(2) Collimator

The x-rays produced by the target material are randomly directed. They form a hemisphere with the target at the centre. In order to get a narrow beam of x-rays the rays generated by the target material are allowed to pass through a collimator which consists of two sets of closely packed metal plates separated by a small gap. The collimator absorbs all the x-rays except the narrow beam that passes between the gaps. A system for achieving a narrow beam of x-rays is shown.



(3) Monochromator

In order to do monochromatization of x-rays two methods are available these are as follows:

(a) Filter

The x ray beam may be partly monochromatized by the insertion of a suitable filter. A filter is a window of material that absorbs undesirable radiation but allow the radiation of required wavelength to pass. This method makes use of the large difference in the mass absorption co-efficient on either side of an absorption edge. An interesting example is the zirconium filter which is used for molybdenum radiation. The relevant spectra are showed in figure. When x-ray emitted from molybdenum is allowed to pass through a zirconium filter, zirconium strongly absorbs the radiation of molybdenum at short wavelengths but weakly absorbs the Kα lines of molybdenum. Thus zirconium allows the Kβ lines to pass. However the continuous or white radiation will also be considerably reduced in intensity. In this case zirconium acts as β filter.

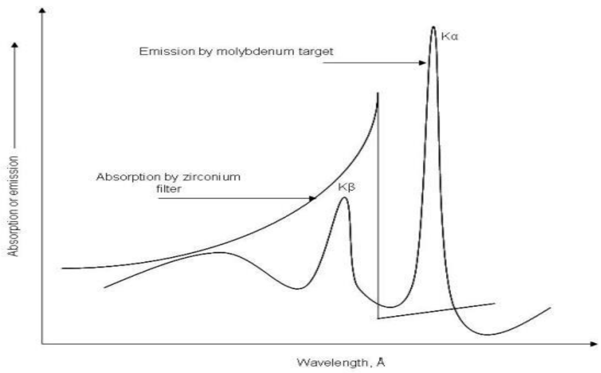


Figure 4: Monochromatic light produce by absorption of unwanted emissions.

(b) Crystal Monochromator

A crystal monochromator is made up of suitable crystalline material positioned in the x-ray beam so that the angle of the reflecting planes satisfied the Bragg's equation ($n\lambda=2d\sin\theta$) for the required wavelength. The beam is split up by the crystalline material into the component wavelengths in the same way as a prism splits up the white light into a rainbow. Such a crystalline substance is called an analysing crystal.

(4) Detectors

The x ray intensities can be measured and recorded either by photographic or counter methods. Both these types of methods depend upon the ability of the x rays to ionize matter and differ only in the subsequent fate of the electrons produce by the ionising process.

(a) Photographic Method

In order to record the position and intensity of the x ray beam a plane or cylindrical film is used. The film after exposing to x rays is developed. The blackening of the developed film is expressed in terms of density units D given by

$D=\log I0/I$

Where I0 and I refer to the incident and transmitted intensities of x rays. The quantity D is related to the total x ray energy that causes the blackening of the photographic film. The value of D is measured by the densitometer.

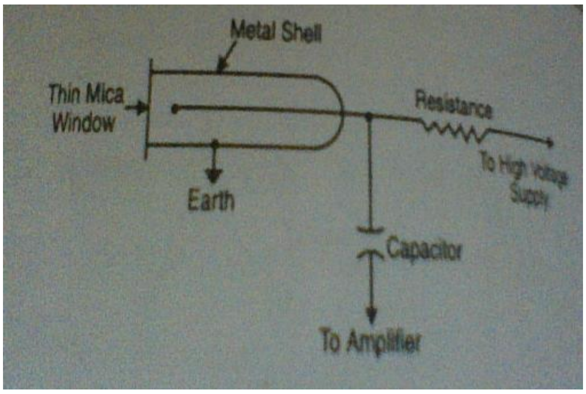
The photographic method is mainly used in diffraction studies since it reveals the entire diffraction pattern on a single film. But this method is time consuming and uses exposures of several hours. At the same time, the photographic method is rarely used for a quantitative measurement because it involves the use of a densitometer, the operation of which can be both time consuming and subject to considerable error.

(b) Counter Methods

These are of the following types.

(1) Geiger Muller Tube Counter

A schematic drawing of a Geiger tube is shown.



The Geiger tube is filled with an inert gas like argon and the central wire anode is maintained at a positive potential of 800-2500 V. When an X-Ray is entering the Geiger tube, this ray undergoes collision with the filling gas, resulting in the production of an ion pair: the electron produce moves towards the central anode while the positive ion moves towards the outer electrode. The electron is accelerated by the potential gradient and causes the ionization of a large number of argon atoms or , resulting in the production of avalanche of electrons that are travelling towards the central anode. This results in an output pulse of 1-10 V which can be measured very easily by employing a simple circuit. The Geiger tube is inexpensive and is relatively trouble free detector. This tube gives the highest signal for a given X-Ray intensity. The various disadvantages are as follows.
(1) The Geiger tube is used for counting low rates.
(2) The Efficiency of the tube falls off rapidly at wavelengths below 1 A0.
(3) As the magnitude of the output pulse does not depend upon the energy of the X-Ray which causes ionization, a Geiger tube cannot be used to measure the energy of the ionizing radiation.

(2) Proportional Counter

Its construction is similar to the Geiger tube counter. A Proportional Counter is filled with a heavier gas like Xenon or Krypton. The heavier gas is preferred because it is easily ionized. A proportional counter is operated at a voltage below the Geiger plateau. The Output pulse of a proportional counter is dependent upon the intensity of the X-Rays falling on a proportional counter. With a proper electronic circuitry one can count X-Rays of a particular energy selectively.

As the dead time of the proportional counter is very short (~0.2 µ), it can be used to count high rates without significant error. This sensitivity and efficiency of a proportional counter are comparable to that of a Geiger tube counter. The advantages of the proportional counters outweigh the extra cost.

(c) Scintillation Detector

In a scintillation detector there is a large sodium iodide crystal activated with a small amount of thallium. When X-Ray is incident upon the crystal, the pulses of visible light are emitted which can be detected by a photomultiplier tube. A schematic diagram of the equipment is shown.

The Scintillation Detector is particularly useful for measuring X-Rays of short wavelengths but its usefulness drops off X-Rays of longer wavelengths.

Crystals used in scintillation detectors include sodium iodide, anthracene, naphthalene, and p-terphenol in xylene.

The dead time of a scintillation counter is short and this allows for counting high rates.

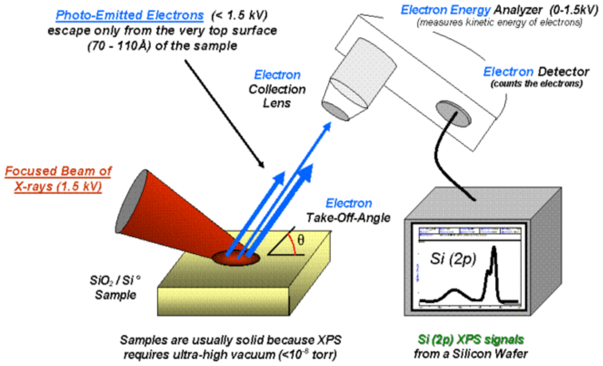
(d) Solid–State Semi Conductor Detector

In this type of detector, the electrons produced by X-Rays Beam are promoted into conduction bands and the current which flows is directly proportional to the incident X-Ray energy.

The main advantage of solid-state semi conductor is that the semi conductor is to be maintained at very low temperatures to minimise the noise and prevent deterioration in the detector characteristics. Most semi conductor detectors consist of a thin layer of n-type material on the surface of a large piece of p-type material.

(e) Semi-Conductor Detectors

Si (Li) and Ge (Li). When an X-Ray falls on a semiconductor or a silicon lithium-drifted detector, it generates an electron (-e) and a hole (+e) in a fashion analogous to the formation of a primary ion pair of a proportional counter. Based on this phenomenon, semiconductor detectors have been developed and are now of prime importance in both X-Ray work and neutron activation analysis. The principle is similar to that of the gas ionization detector are used in a proportional counter, except that the materials that are used in a solid state. A schematic diagram of a silicon lithium-drifted detector is shown. In this system, a very pure silicon block is setup with a thin film of lithium metal plated onto one end. The density of free electrons in the silicon is very low, constituting a p-type semiconductor. Semiconductors detectors always operate with a combination of these two types.



Under the influences of an applied voltage the electrons move toward the positive charge and the holes toward the negative charge. The voltage generated is a measure of the X-Ray intensity falling on the crystal. The process is analogous to that of the proportional counter. Upon arriving at the lithium coating, a pulse is generated. The voltage of the pulse equals Q/C where Q is the total charge collected on the electrodes and C is the detector capacity. The number of pulses is the direct measure of the number of X-Ray photons falling on the detector, which now provides a method of measuring X-Ray intensity.

Silicon lithium-drifted detectors are widely used. Semiconductor detectors may also be made with the germanium as the principal metal and doped with other elements in group 3A of the periodic table such as gallium. The efficiency of the detector may be further increased by cooling the silicon (or germanium) at low temperatures such as that of liquid nitrogen. This increases the resistance of the silicon when unexposed to radiation, and therefore the contrast when radiation falls on a detector is greater. Low temperatures also prevent the lithium from precipitating out.

Working

The general arrangement for a dispersive X-Ray absorption method is shown. This has been put in the market by General Electric Company.

In this apparatus, a tungsten X-Ray tube is employed which operates at 15-45 KV. A synchronous motor-driven chopper is kept between the cell and attenuator which alternately interrupts one-half of the X-Ray beams. Between the chopper and reference sample compartment, there is a variable thickness aluminium attenuator (in the shape of a wedge). There are duplicate reference and sample cells up to 65 cm in length. If liquids and gases are to be analysed, there are special arrangements for continuous flow of process streams. Both halves of X-Rays beam are allowed to fall on a common phosphor-coated photomultiplier tube which is protected from visible light by a thin metallic filter.

First of all, a reference sample is kept in the reference cell whereas the sample to be analysis is kept in the sample cell. Then, the adjustment is made in the attenuator until the absorption in the two X-Rays Beams is brought into balance. The change in thickness of aluminium required for different samples is a function of the difference in composition.

In most of the samples to be analysed, a calibration curve is prepared. Then the unknown concentration of the sample to be analysed is obtained from the calibration curve.

Applications

1. It has been used to determine chlorine in hydrogen, plastic and hydrocarbons.
2. It has been used to determine barium fluoride in carbon and barium or lead in special glass.
3. This has been used to locate trace elements, such as barium and iodine in the body. These elements are taken by the patients. Then their movements in the body are followed by x-ray absorption. This method helps the doctor to detect the activity of the body tissues towards barium or iodine.
4. This has been used to detect the impurities such as oxides in welds and other joints.
5. This has been widely used to measure the volume of the liquids in closed vessels or pipes without opening or breaking the vessels or pipes.
6. It is used in determination of lead in gasoline.
7. Another application of x-ray absorption medicine is to define the shapes of veins and capillaries.

Future Advancement: The XPS market is likely to grow at a healthy pace with the rise in the research activities in the medical sector. The increase in the number of players and the rising investments to introduce safe and pure drugs is further projected to ensure the development of the market in the coming years. The rising demand for effective drugs and minimal medication error is expected to encourage the growth of global XPS market in the next few years. Increasing applications of XPS systems in medical research and drug safety will augment the industry growth in forthcoming years. Technologically advanced XPS systems are highly preferred by researchers and scientists in discovering drugs for chronic diseases such as cancer. Recent developments such as anti cancer nano particles will increase the demand for x ray photoelectron spectroscopy techniques. Furthermore, XPS systems are also utilized in the treatment of bone disorders. XPS systems offer efficient surface characterization of artificial ligaments utilized during surgical procedures that should augment the industry growth.

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