

In practice, this would lead to a variation in the observed energy of the ejected electrons and erroneous results would be derived. It is therefore highly desirable to eliminate this variable charge.

This problem can be overcome by flooding the surface of the sample with low-energy electrons, which neutralize the positive charge built up on the surface. This is done by using an electron flood gun. Of course, these electrons in turn affect the work function of the surface to some extent, but the effect is constant and reproducible data are obtainable over an extended period of time.

#### 14.2.1.1.6 Ion Gun

An ion gun is used in XPS and Auger instruments for two purposes: (1) to clean the sample surface of any external contamination layer and (2) to sputter atoms from the surface in order to obtain a depth profile analysis, discussed under applications. One type of ion gun uses a heated filament to ionize inert gas atoms. The ions are accelerated by a potential placed on the ionization chamber and are focused to strike the sample surface. The ions remove atoms from the sample surface by collision. The rate of removal of surface atoms is controlled by the kinetic energy of the ions and by the nature of the surface atoms; sputtering rates may be as high as 10 nm/min.

#### 14.2.1.1.7 UHV System

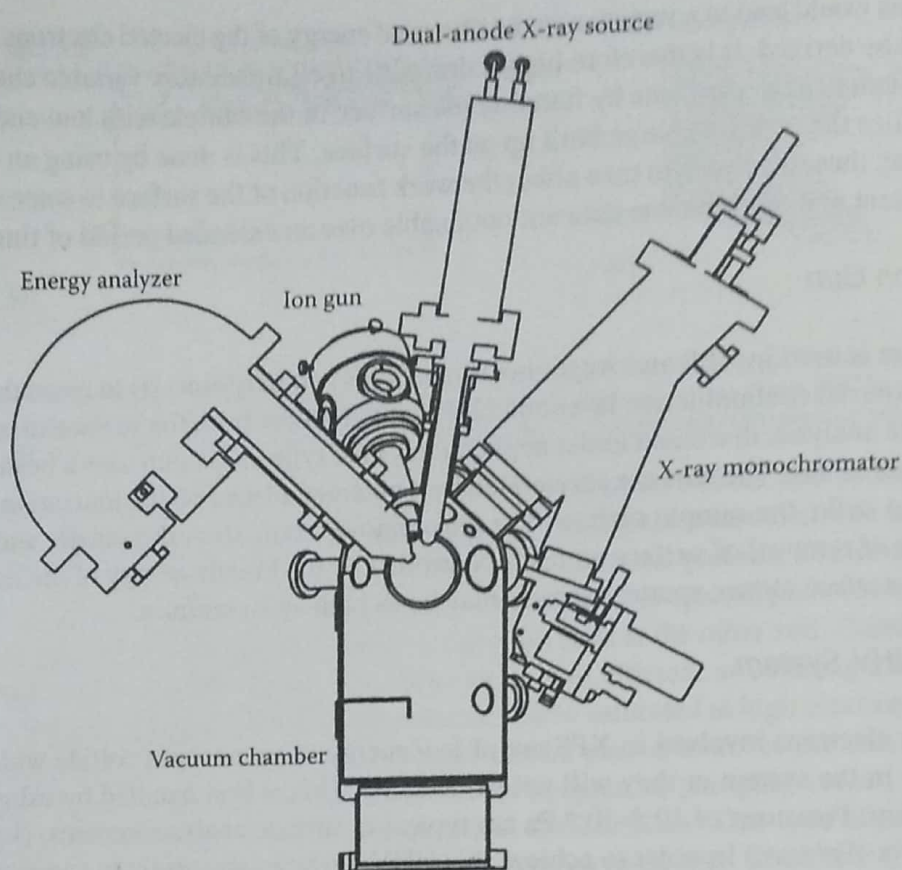
Since the electrons involved in XPS are of low energy, they must not collide with other atoms or molecules in the system or they will not be detected. This is best handled by using a very high vacuum system. Pressures of  $10^{-8}$ – $10^{-9}$  Pa are typical in surface analysis systems. (1 pascal, Pa, is equal to  $7.50 \times 10^{-3}$  torr.) In order to achieve this UHV, surface analysis instruments are fabricated of stainless steel. Stainless steel structures can be evacuated to the required low pressure with the appropriate combination of vacuum pumps. The stainless steel can also be heated ("baked out") to remove adsorbed gases. Other required components such as windows and gaskets must be made of materials that do not outgas and can withstand required elevated temperatures. The vacuum pumps used in surface analysis instruments to achieve the UHV pressures required include turbomolecular pumps, ion pumps, cryopumps, and oil diffusion pumps. Oil diffusion pumps must include a liquid nitrogen trap to prevent oil vapor from entering the instrument. Details of materials used in surface analysis systems and the vacuum pumps used can be found in the handbook by Ewing listed in the bibliography and references therein.

As we will see, surface analysis equipment is very similar for several techniques, so most surface analysis instruments are configured for multiple surface analysis techniques. A schematic diagram of a commercial instrument showing the placement of the ion gun, energy analyzer, source, and so on is shown in Figure 14.8.

#### 14.2.1.2 Sample Introduction and Handling for Surface Analysis

The sample must be kept under high vacuum during analysis. In older instruments and some modern lower-cost instruments, the main analysis chamber must be brought to atmospheric pressure in order to insert or change the sample. The system is vented with nitrogen, the sample inserted, and the entire system pumped down to UHV pressures again before analysis can begin. This presents a problem when numerous samples are to be analyzed. Many instruments utilize sample prechambers, small-volume compartments that will accommodate a number of samples and can be evacuated rapidly. The samples are then transferred into the main chamber without causing an excessive rise in pressure.

Sample holders range from those that accommodate samples of 1–2 cm diameter and about 1 cm in thickness to custom-designed sample chambers that can hold much bigger samples and those that are of irregular size and shape. Chambers designed for 95 mm diameter computer hard disks are



**Figure 14.8** A schematic diagram of a commercial surface analysis instrument, the PHI Model 5600 MultiTechnique system. The monochromatic X-ray source is located perpendicular to the sample surface (not shown); the standard X-ray source is at  $57.4^\circ$  relative to the analyzer axis. (From Moulder, J.F. et al., In *Handbook of X-Ray Photoelectron Spectroscopy*. Chastian, J. and King, R.C., eds., Physical Electronics, Inc., Eden Prairie, MN, 1995; Courtesy of Physical Electronics, Inc., Eden Prairie, MN, [www.phl.com](http://www.phl.com).)

common, for example. The sample in its holder is placed on a stage that can be moved in all directions and allows the sample to be rotated and tilted for optimal positioning. The stage in a modern surface analysis instrument is under computer control. Some sample stages allow the sample to be heated or cooled as necessary. Cooling, for example, is required to analyze materials with a high vapor pressure, when volatile surface components are to be studied and for samples such as plastics that outgas at room temperature under UHV conditions.

XPS performed with commercial instruments as described is used for the analysis of the surfaces of solid samples. The solid must be in electrical contact with the spectrometer, so conducting solids are easily analyzed. Nonconductive samples can be analyzed by using a low current electron flood gun or a combination of electron flood gun and ion gun to neutralize the surface charge of an insulator. Solid samples can be analyzed "as is," but they often must be cut to fit the sample holder. Due to the surface sensitivity of XPS and AES, great care must be taken when handling samples to prevent unwanted contamination of the sample surface. The analyst should avoid touching the sample, using solvents that may leave a residue or solvents that remove material of interest from the surface. Dust and particulates from sample cutting or cleaving are typically removed using an inert gas such as nitrogen. Sample handling tools should be cleaned using high-purity solvents. Analysts should wear gloves that are powder free and silicone free. Because of the surface sensitivity of these techniques, it is common to detect atmospheric or environmental contaminants on the sample surface. Common contaminants include hydrocarbons and thin oxide layers on the surface of metal samples. Sometimes, these surface layers may be of analytical interest, as they may be related to the

processing used to create the sample. If they are not of interest, organic contaminants are removed with high-purity solvents, and oxide layers are removed by sputtering the sample in the instrument. An exposed chemically active surface must be kept under UHV to prevent rapid contamination of the surface.

Even under vacuum, gas molecules will reabsorb onto a clean sample surface. Hercules and Hercules describe that at pressures between  $10^{-8}$  and  $10^{-10}$  torr, a surface can be covered by a monolayer of adsorbed gas molecules in from 1 to 10 h, while at  $10^{-6}$  torr, the same process occurs in a few seconds. This rapid recontamination of a cleaned surface makes clear the need for UHV conditions for accurate surface analysis.

Some surface analysis instruments are equipped with apparatus to fracture or cleave a material within the UHV chamber to expose a fresh surface for analysis. Metal samples are routinely fractured in UHV to expose grain boundaries. This permits XPS or AES detection of bulk impurities that have segregated to grain boundaries, for example. Grain boundary chemistry is of great interest to metallurgists for many reasons. As noted, even under UHV conditions, a limited time is available for contamination-free analysis of freshly exposed surfaces.

### 14.2.1.3 Analytical Applications of XPS

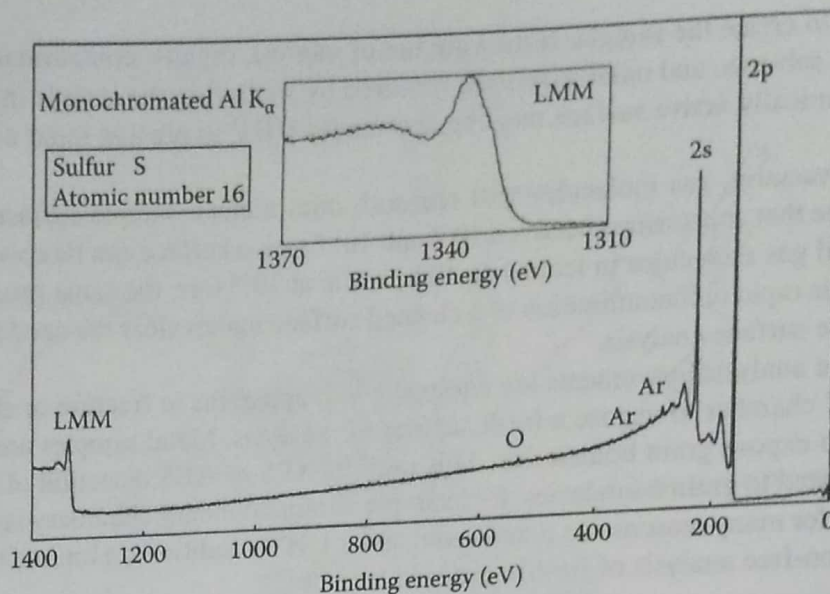
Fundamental research in physical chemistry using XPS has included the study of gases and liquids to explore the energies of valence electrons, radicals, excited states, vibrational states, and more, but a discussion of this is beyond the scope of this text. Only the analysis of solid surfaces will be considered. For qualitative elemental analysis and especially for a "first pass" at an unknown sample, a wide energy range "survey" spectrum should be collected. In order to obtain chemical state information, and for quantitative analysis of minor elements, a higher-resolution detail scan is taken of the energy regions of interest. Detail scans must be collected with a sufficient signal-to-noise ratio so that accurate peak positions and peak areas can be determined. The sampling depth for most materials is a few atomic layers.

Tables 14.2 and 14.3 provide examples of applications of surface analysis techniques. XPS can be used for many of these applications.

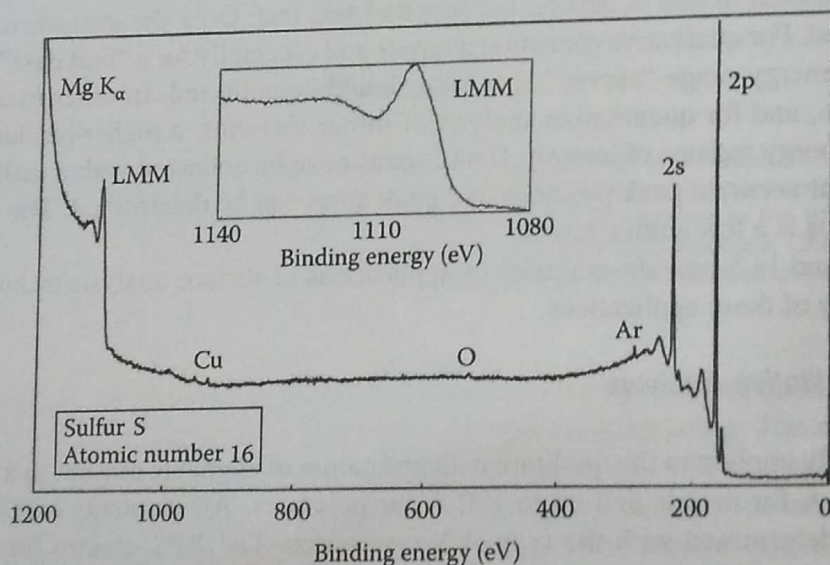
#### 14.2.1.3.1 Qualitative Analysis

XPS is readily applied to the qualitative identification of elements present in a sample surface, to depths of 25 Å for metals and up to 100 Å for polymers. All elements except hydrogen and helium can be determined with the typical X-ray source. The XPS spectra for sulfur obtained with monochromated Al  $K_{\alpha}$  radiation and Mg  $K_{\alpha}$  radiation are presented in Figures 14.9 and 14.10, respectively. Each spectrum consists of a limited number of photoelectron peaks in the range of 0–1400 eV in binding energy for Al (0–1200 eV for Mg). XPS photoelectron peaks from the sulfur 2s (K shell) and 2p (L shell) orbitals are seen, as well as an Auger peak (marked LMM). Some small contaminant peaks from Ar and oxygen can be seen in the spectra. Auger peaks can be distinguished from photoelectron (XPS) peaks. Because Auger electron kinetic energies are independent of the ionizing radiation energy, on a plot of binding energies, the Auger lines appear to be at different positions when different X-ray sources are used. The Auger peak is shown as an inset in each of the two spectra; as you can see, the Auger peak appears at a higher binding energy when Al X-radiation is used than when Mg X-radiation is used. The XPS peaks do not change position. Figures 14.9 and 14.10 are survey spectra, the type of scan that would be used for qualitative elemental analysis of an unknown.

For low atomic weight elements ( $Z < 30$ ), energy peaks are observable corresponding to the K and L shells (the s and p electrons). For elements with atomic numbers between 35 and 70, the d electrons result in peaks in the XPS spectrum. For elements with atomic numbers greater than 70,



**Figure 14.9** XPS spectrum of sulfur collected with monochromated Al  $K_{\alpha}$  radiation. (From Moulder, J.F. et al., In *Handbook of X-ray Photoelectron Spectroscopy*, Chastian, J. and King, R.C., eds., Physical Electronics, Inc., Eden Prairie, MN, 1995; Courtesy of Physical Electronics, Eden Prairie, MN, Inc., www.phl.com.)



**Figure 14.10** XPS spectrum of sulfur collected with Mg  $K_{\alpha}$  radiation. (From Moulder, J.F. et al., In *Handbook of X-ray Photoelectron Spectroscopy*, Chastian, J. and King, R.C., eds., Physical Electronics, Inc., Eden Prairie, MN, 1995; Courtesy of Physical Electronics, Inc., Eden Prairie, MN, www.phl.com.)

the pattern includes f electrons. It can be seen that qualitative identification of the surface elements present is possible based on identification of the binding energies. Binding energies for all elements are tabulated and may be found in the NIST XPS database at <http://www.nist.gov/srd/surface> and in tables in references such as Moulder et al. (1995) listed in the bibliography. Typical data for S and Cu are shown in Figure 14.11. In addition, the spin doublet patterns and ratios for the lines from the p, d, and f electrons are characteristic and also tabulated. The copper XPS spectrum is shown in Figure 14.12. The spin doublet for the 2p electrons is seen ( $2p_{1/2}$  and  $2p_{3/2}$ ), and the ratio of the lines is about 1:2, which is the expected intensity ratio for these lines. XPS lines from the 2s, 3s, 3p, and 3d orbitals are also seen, along with the Auger LMM transition.

|  |  |  |  |                   |                   |
|--|--|--|--|-------------------|-------------------|
| Line positions (eV)  |  |  |  |                   |                   |
| Photoelectron lines  |  |  |  |                   |                   |
| 2s   | 2p <sub>1/2</sub>  | 2p <sub>3/2</sub>  | 3s   |                   |                   |
| 228  | 165  | 164  |  |                   |                   |
| Auger lines  |  |  |  |                   |                   |
| L <sub>23</sub> M <sub>23</sub> M <sub>23</sub>                  |  |  |  |                   |                   |
| 1336   | (Al)   |  |  |                   |                   |
| 1103   | (Mg)   |  |  |                   |                   |
| Line positions (eV)  |  |  |  |                   |                   |
| Photoelectron lines  |  |  |  |                   |                   |
| 2s   | 2p <sub>1/2</sub>  | 2p <sub>3/2</sub>  | 3s   | 3p <sub>1/2</sub> | 3p <sub>3/2</sub> |
| 1097   | 953  | 933  | 123  | 77                | 75                |
| Auger lines  |  |  |  |                   |                   |
| L <sub>3</sub> M <sub>23</sub> M <sub>23</sub>                   | L <sub>2</sub> M <sub>23</sub> M <sub>23</sub>                   | L <sub>3</sub> M <sub>23</sub> M <sub>45</sub> ( <sup>1</sup> P) |  |                   |                   |
| 719  | 712  | 648  | (Al)   |                   |                   |
| 486  | 479  | 415  | (Mg)   |                   |                   |
| L <sub>3</sub> M <sub>23</sub> M <sub>45</sub> ( <sup>3</sup> P) | L <sub>2</sub> M <sub>23</sub> M <sub>45</sub> ( <sup>1</sup> P) | L <sub>3</sub> M <sub>45</sub> M <sub>45</sub>                   | L <sub>2</sub> M <sub>45</sub> M <sub>45</sub> |                   |                   |
| 640  | 628  | 568  | 548  | (Al)              |                   |
| 407  | 395  | 335  | 315  | (Mg)              |                   |

Figure 14.11 Typical XPS data tables from literature references. (Top) Data for sulfur; (bottom) data for copper. (From Moulder, J.F. et al., In *Handbook of X-Ray Photoelectron Spectroscopy*, Chastian, J. and King, R.C., eds., Physical Electronics, Inc., Eden Prairie, MN, 1995; Courtesy of Physical Electronics, Inc., Eden Prairie, MN, www.phi.com.)

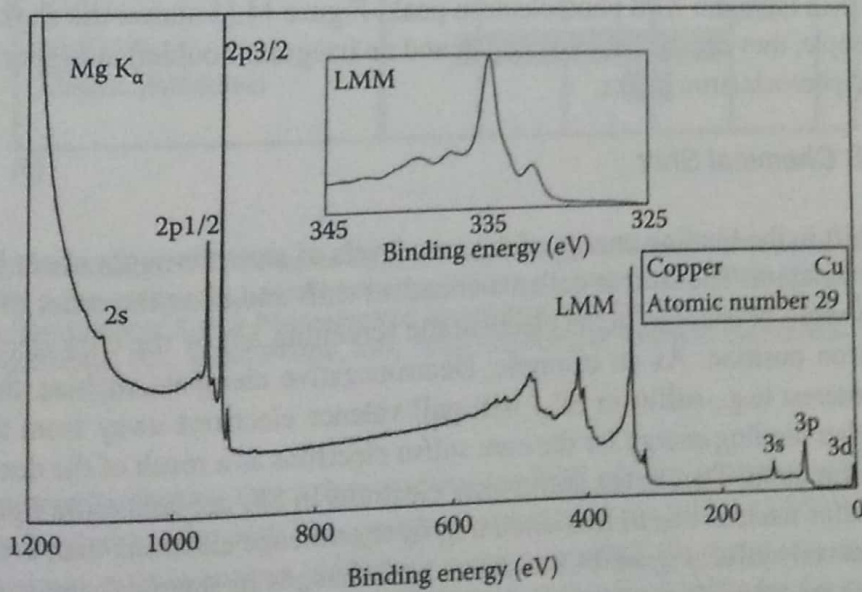
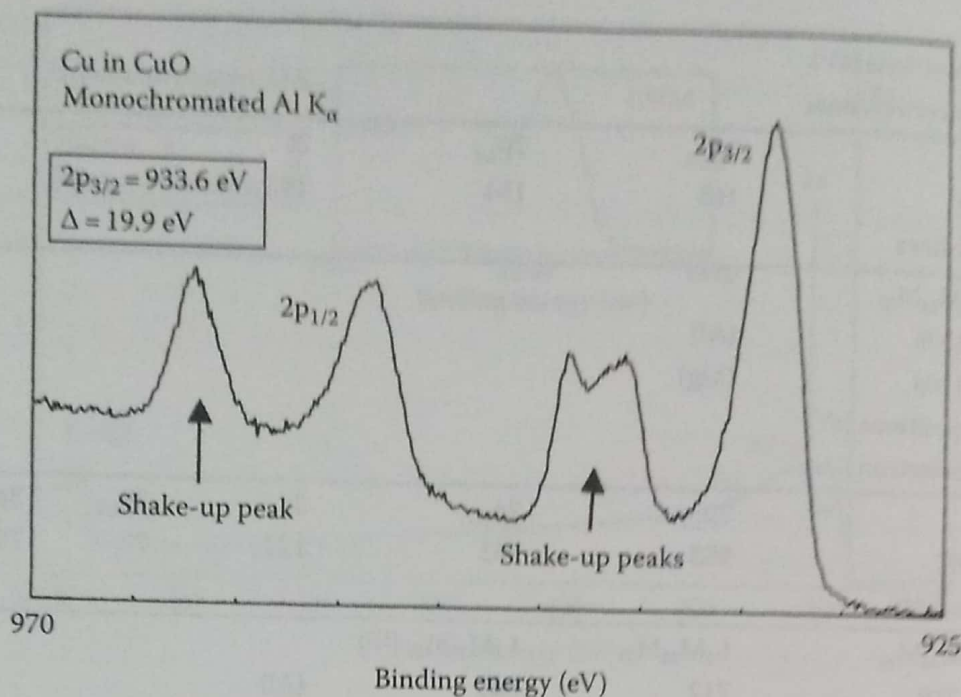


Figure 14.12 The XPS spectrum of copper collected with Mg K<sub>α</sub> radiation. (From Moulder, J.F. et al., In *Handbook of X-Ray Photoelectron Spectroscopy*, Chastian, J. and King, R.C., eds., Physical Electronics, Inc., Eden Prairie, MN, 1995; Courtesy of Physical Electronics, Inc., Eden Prairie, MN, www.phi.com.)



**Figure 14.13** “Shake-up” peaks in the copper XPS spectrum of a copper oxide sample. These peaks are one example of several processes that result in lines other than XPS and Auger lines in an XPS spectrum. (Modified from Moulder, J.F. et al., In *Handbook of X-Ray Photoelectron Spectroscopy*, Chastian, J. and King, R.C., eds., Physical Electronics, Inc., Eden Prairie, MN, 1995; Courtesy of Physical Electronics, Inc., Eden Prairie, MN, [www.phl.com](http://www.phl.com).)

XPS spectra also exhibit some minor peaks due to a number of other processes. Small peaks called X-ray satellite peaks can appear at lower binding energies due to the nonmonochromatic nature of the X-ray source. X-ray “ghost peaks” occur due to other elements present in the X-ray source; Cu lines in spectra are an example of these ghost peaks. Copper is the base material used in the X-ray anode, so Cu lines may appear in the spectra of samples that contain no Cu. A complex photoelectric process results in “shake-up” peaks, which are peaks that occur slightly higher in binding energy than the main XPS photoelectron peak. Figure 14.13 shows the shake-up peaks in a copper oxide sample; they are the peaks (a singlet and an irregular doublet) at higher binding energy than the marked photoelectron peaks.