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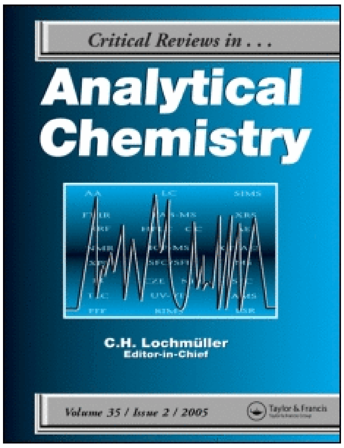

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APPLICATIONS OF PHOTOELECTRON SPECTROSCOPY TO ANALYTICAL CHEMISTRY

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I. INTRODUCTION

Since 1940 many spectroscopic techniques have been discovered and refined to further investigations into the electronic structure of atoms and molecules. Most of these, however, measure differences in absorption of electromagnetic energy of various wavelengths which are in turn related to atomic or molecular phenomena. In photoelectron spectroscopy and related techniques (Auger, Electron Impact, and Penning Ionization) a liberated ejected electron is examined. Therefore, the technique is sensitive to ionization processes and the parameters governing electron-molecule interaction. It thus provides a separate and distinctly unique approach to probing electronic structure.

The subject of photoelectron spectroscopy is divided, at the present time, into two somewhat separated areas according to the energy used to induce photoelectron emission. Within the context of electron spectroscopy, the older of the methods is based on the use of X-rays as a source of excitation. In 1914 Robinson[1] built a low-resolution instrument for the purpose of measuring the kinetic energies of photoelectrons ejected by X-ray absorption. The spectra obtained did not give the resolution necessary for accurate measurement of the kinetic energies, and the technique lay dormant until the early 1950's, at which time a prototype spectrometer was built by Siegbahn and Edvardson.[2]

The first results of analytical significance were published by Steinhardt and Serfass[3] in 1951; however, it was not until the middle 1960's that much interest was shown in the field. At this time two research groups were well-established, one led by Siegbahn in Sweden and one by Turner in England. Turner's group was the first to make use of vacuum ultraviolet radiation as it applies to photoelectron spectroscopy.

The division between the two domains, depending on the source of excitations, may gradually become less distinct with the advent of the continuously variable monochromatic synchrotron radiation. In the future a distinction may result with a broader line set by the photon energy required to excite core or valence electron lines from all elements.[15] The application of synchrotron radiation will sooner or later stimulate new extensions of electron spectroscopy. Of course, most of the basic applications can be accomplished with the present instrumentation using further improvements, without need for a synchrotron.

Electron spectroscopy is sensitive to every element except hydrogen and helium and thus can play an important role in all phases of chemistry. Its greatest impact has been two-fold. First, since the electronic energy levels of atoms are sensitive to their environment, the technique is the best available for determining oxidation states of atoms in molecules. Secondly, from the photoelectron spectra one can obtain the relative ratios of different elements and different atoms of the same element. The technique, however, only samples the first few angstroms of a solid surface. This is both good and bad. On the bad side, great care must be taken in sample preparation in order to keep the surface clean and, if possible, representative of the bulk sample. On the good side, this makes the technique sensitive to many important areas of research such as corrosion studies, catalysis, semiconductor studies, adsorbed gas work, and electrode studies.

The ultraviolet source has, at the present time, its main application in gas phase work with emphasis on studies that are more theoretical in nature. It does, however, have analytical applications that have not been fully exploited. Work on the link-up of gas chromatography with electron spectroscopy has only just begun and shows promise in areas such as analysis of reaction products and other types of gaseous mixtures.

At the moment, instrumental design is being improved with an eye toward better sensitivity and resolution. Recent development of the chevron plate electron detector offers faster counting. The application of Vidicon[4] and resistive strip[5] techniques have been reported. When the problems of sensitivity and resolution are overcome one can expect photoelectron spectroscopy to rank among the top chemical research tools and to be an accurate quantitative technique.

This review was made much easier by the several books[6-9] and excellent review articles[10-15] that have been published in the last five years. An attempt is made here to review all pertinent literature, and *Chemical Abstracts* was searched from 1965 to the first issue of November 1974.

II. X-RAY (XPS OR ESCA)

A. Surface Analysis

Problems involving surface analysis fall into several categories. For problems requiring oxidation state information as well as elemental composition, XPS is the method of choice. XPS is a nondestructive technique having sensitivity of 1.0% for the bulk material and 10^{-8} to 10^{-9} g or 10 to 0.01 monolayers. A sample area of a few mm^2 in a vacuum of 10^{-5} to 10^{-10} torr may be analyzed. The analysis time may be a few minutes to several hours. It can characterize thin films, catalytic surfaces, corrosion, and identify surface contaminants and polymer modifications.

Sensitivity – The aspects that should be considered in the study of surface species are the following: (a) escape depth (i.e., how thick a surface slice contributes to the signal); (b) total signal response (i.e., how rapidly one can detect a signal); (c) quantitative spectrum; (d) degree of chemical information; (e) surface changes as a result of photon interaction. These aspects have been discussed by Brundle.[16,22]

Escape depths – Upon irradiation only those electrons ejected which do not lose energy by inelastic scattering on their passage to the surface will appear in the kinetic energy (KE) spectrum at their original characteristic positions. The rest contribute to the discrete and continuum background at lower KE. When assessing escape depths, l (the mean free path) is employed. Factors affecting l are discussed.[17]

The mean free path length is expected and found to be highly dependent on kinetic energy; it falls rapidly until reaching a minimum at approximately 100 eV, then increases. The actual position of the curve on the l axis will depend on the material, but for metals values of only a few angstroms are expected somewhere within the 10- to 1,000-eV range. Brundle[16] has summarized the available experimental results on l in Figure 1. A similar curve was reported by Tripathi and Clark.[40]

1. Total Signal Response

A technique which probed solely the first atomic layer but took a long time to obtain the necessary data would be of little use (i.e., a technique with a sufficiently high signal/noise ratio in addition to signal/background ratio is desired). A reasonable length of time for the measurement requirement depends on the situation. For a gold surface at 1×10^{-10} torr, it could be as long as one is patient. For a reactive metal where an adsorbed phase/gas phase exchange at 10% coverage is being followed, it may be only a few seconds.

Under the conventional instrumental conditions now used for each technique, AES (Anger electron spectroscopy) is far superior in terms of the speed of detection, under typical conditions, to scan a clean gold surface, giving recording times for AES, XPS, and UPS as 80, 2,000, and 300 sec, respectively.

2. Quantitative Spectrum

Despite the theoretical possibility of distinguishing between surface and substrate species in XPS by correlating signal intensities with the X-ray photon energy ($h\nu$) or the angle of photoelectron emission with respect to the plane of the surface (θ), no more than a broad qualitative distinction is obtained. UPS has not been used in quanititative application. XPS was reported as a quantitative tool more than 20 years ago for analyzing alloys based on calibration techniques.[3] AES and XPS alone are not yet capable of providing quantitative depth profile, either in relative or absolute terms. For uniform condensate layers on a uniform substrate, absolute measurements could be made by XPS if flux, cross sections, transmissions functions, etc. were known accurately. Calibration techniques are normal and can be quite accurate in favorable cases, especially in the submonolayer range. Relative element concentration calibrations can be extracted from such submonolayer studies or from uniform bulk compounds of known composition.

3. Chemical Information

Most of the chemical information available from XPS is based on chemical shift data. There is a wealth of data now existing on the use of chemical shifts in XPS to study bonding both in the solid and gas states. Monochromatic X-ray sources can reduce the instrumental contribution to approximately 0.3 eV. Core level natural linewidths (lifetime controlled) are often beyond 0.5 eV for solids. When using a nonmonochromatic X-ray source, therefore, chemical shifts of $\geqslant 0.3$ eV may be detected with some confidence in solids when fairly sharp lines are available, but claims beyond this should be treated with caution. Deconvolution of poorly resolved component lines is becoming popular and may be chemically valid if the number of inequivalent identical atoms contributing to the band envelop is already known. In $CH_3CH_2COOCF_3$ an unresolved C (1s) envelope can only contain four 1s carbon lines of approximately equal intensity. The existence of satellite lines complicates the situation in many cases due to the possibility of multiple splitting or multiple excitation.[18,19] Spin coupling of the core hole state with unpaired electrons in the valence levels, and/or with orbital angular momentum of the residual electrons, results in a variety of possible ion energy states. These effects are often chemically dependent, and it may not be easy to distinguish between them and chemical shifts; if both are present, it is difficult to resolve them experimentally. Satellite structure can provide valuable additional information about chemical bonding.[18]

Complications are frequently encountered when the general case is applied to the surface case due to the following facts: (1) low surface signal intensity; (2) lines contributed from the under-

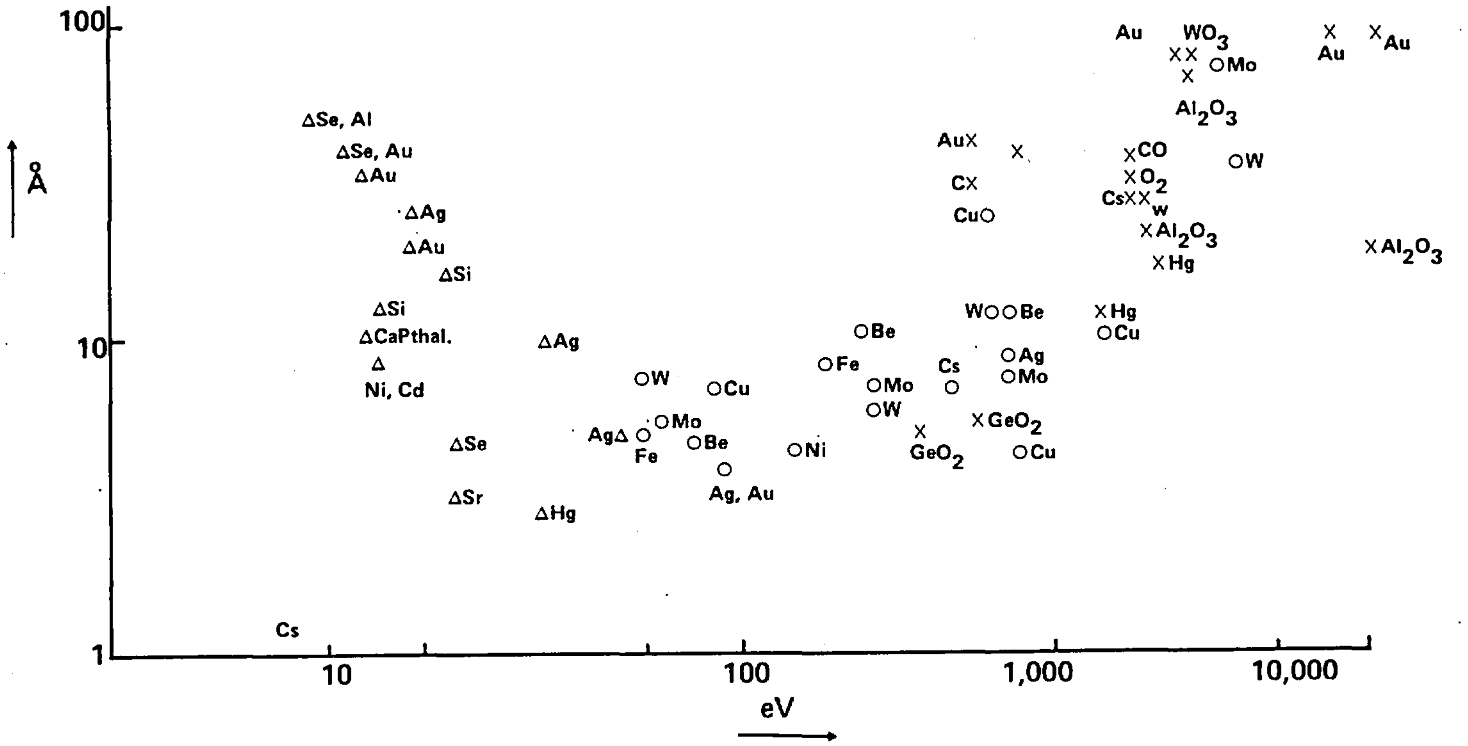


FIGURE 1. Experimental determinations of *l* in XPS (X), UPS (O), and AES (Δ). (From Brundle, C. R., *J. Vac. Sci. Technol.*, 11, 212 (1974). With permission.)

lying bulk with relatively long mean free path; (3) lack of supporting backlog of information on chemical shifts for surfaces to help interpretation; and (4) lack of reliability of deconvolution procedures.

Surface studies in XPS literature refer mostly to fairly thick and often ill-defined surface phases. It has been suggested that core level binding energies should be lower in the surface layer on account of their reduced coordination.[20,21] Since mean escape depths are of the order of 20 Å for several metals, for one KeV electron energy about 90% of the XPS line intensity should be contibuted by approximately a 15-monolayer depth of the "thick surface." The first monolayer may only contribute about 15% of this line intensity. For clean metal surfaces broadened XPS peaks should, therefore, be observed if the reduced coordination theory is correct. No experimental evidence has yet been given for this. The Au 4f, Mo 3d, and W 4f levels in clean polycrystalline samples all exhibit symmetrical XPS peaks of 1.2 eV width or less, which can only be accounted for by the indifferent effective electronic environment of the atoms through the first several monolayers.[22,23] This means that coordination effects, if any, are insignificant. It is also possible that chemisorption at metal surfaces shows little effect on the bonding energies of the surface metal atoms. For instance, no detectable shift was observed during the absorption of carbon monoxide on molybdenum metal since the Mo 3d lines only showed a slight decrease in intensity and a marginal broadening (Figure 2). Similar results are observed for chemisorption studies of Mo/O_2,[16] W/CO,[24] W/O_2,[24] Fe/O_2,[16] and Ni/O_2.[16] Kim and Winograde,[25] however, reported a small chemically shifted (~0.7 eV) component, which can be extracted by deconvolution from the Pb $4f_{7/2}$ profile, in the Pb/O_2 chemisorption system using monochromatic x-rays. This cannot be confirmed from nonmonochromatic studies.[16] Therefore, if genuine, small effects could be undetectable in the above examples. Chemical shifts of metal substrate peaks on adsorption are generally considered to be small or nonexistent, in contrast to the considerable shifts observed on the formation of thick surface phases (Table 1). This implies that the electron transfer from the adsorbate is "soaked up" by the substrate lattice so that the effect by each surface substrate atom is small.[16] Then the reliability of a report that CO adsorption on Pt produces a Pt $4f_{1/2}$ shift of 2 eV[29] and that the substrate Pt signal vanishes has been questioned.[16] Further experimental results with various metals and nonmetals will clear up the controversy.

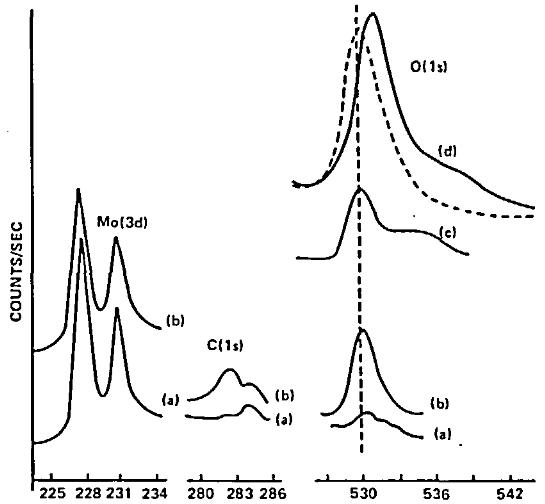


FIGURE 2(a). XPS spectrum of a molybdenum film. Recording data: Mo 3rd region, 20-eV analyzing energy, 500-W X-ray power, 200-sec scan time; C 1s region, 500-eV analyzing energy, 150-sec scan time; O 1s region, 50-eV analyzing energy, 100-sec scan time. (b) Spectrum of film plus RT adsorbed CO. Data as for (a). (c) Film of (b) cooled to 80°K plus further CO adsorption; O 1s region spectrum, 50-eV analyzing energy. (d) Clean Mo film cooled to 80°K, followed by CO adsorption; O 1s region, 100-eV analyzing energy. Dotted trace is the spectrum after warming to RT. [Trace (d) is a lower resolution higher sensitivity spectrum than traces (a), (b), and (c).]

TABLE 1

Chemical Shifts Metal Substrate Caused by Oxidation

Metal	Oxidation to	Lines	Extent of shift, eV	Ref.
W	WO_3	W 4f	≅ 4	12
Mo	MoO_2	Mo 3d	≅ 3	13
Mo	MoO_2	Mo 3d	≅ 4	1
Al	Al_2O_3	Al2s	≅ 2.5	14

For a single layer of adsorbate there is no lattice to soak up the electron transfer effects, and larger chemical shifts will occur. Thus, different chemisorption processes of a molecule which occur at different coverages and/or temperatures may be distinguished[23,24] (see Figure 2). There is an interesting O 1s region in the Mo/CO system. After room-temperature adsorption has stopped and the Mo is cooled to 80°K in the presence of CO[23] (see Figure 2, trace c), a distinct additional band is observed which is so broad as to indicate that a new "state" of chemisorption must be considered. That is either a collection of molecules with a variety of heats of adsorption or a superimposition of two or more discrete states. Similar work with tungsten has distinguished the α and β states of CO.[24] For the Mo/CO system, if the adsorption begins at 80°K instead of room temperature, a different state is observed (Figure 2, trace d). This state may be considered as the equivalent of the "virgin" CO state on tungsten.[30]

4. Application of XPS to Surface Problems

a. Pollutant Analysis

Hulett et al.[31] studied sulfur compounds adsorbed onto smoke particles and fly ash and determined the oxidation state of S for the adsorbed sulfur compounds. The sulfur compounds under study were present mostly as an adsorbed layer on the particles. Spectral analysis indicated the presence of two kinds of sulfur in the fly ash, which were postulated to be the sulfate or adsorbed sulfur trioxide. The smoke particles contained three types of sulfur; the XPS spectra indicated the presence of $SO_3^=$, $SO_4^=$, and H_2S or a mercaptan. The types of sulfur adsorbed on the particles depend on the nature of the particulate matter and other factors.

b. Surface Oxides

Various species of the NiO system, such as Ni, NiO_{ads}, NiO, Ni_2O_3, and $NiOO_{ads}$, have been studied by XPS.[19] Ni_2O_3 is formed by oxidation of Ni at temperatures < 250°C and is present on the surface of ordinary NiO.

The oxide species on metals of Mo,[16,23,33,36] W,[16,24,26,37,38] and Al[28,39,12,45,46] have been widely studied. The XPS spectra of magnesium,[40] vanadium,[41] lead,[42] carbon,[43] iron,[44,45] chromium,[46] and copper[47] have also been investigated.

c. Adsorption

Definitive interpretation of many surface phenomena on an atomic level often requires a knowledge of the chemical composition of the surface and the oxidation state of the surface atoms. Both UPS and XPS are suitable for studying the oxidation states and chemisorption. The application of XPS to studies of chemisorption on metals has been relatively slow for at least two reasons. First, the instrument with high sensitivity and ultrahigh vacuum is still lacking, and secondly, there was somewhat slow acceptance since there were no fundamental reasons for the technique being less suitable for surface studies than Auger electron spectroscopy (AES), which had been widely and quickly accepted as essentially a surface technique. Now the ultrahigh vacuum electron spectrometers are commercially available, and studies with an ultrahigh vacuum electron spectrometer have been reported.[16,22,23,47]

Evans et al.[47] compared the photoelectron spectra of clean metal surfaces with those exposed to molecular oxygen. For a silver surface, an unmistakable O 1s signal was produced; this could be removed by appropriate cleaning. Upon admission of excited (by microwave discharge) oxygen, consisting of an unknown mixture of atomic and molecularly excited oxygen, the O 1s signal changed dramatically (Figure 3), with the new narrow peak being assigned to a less strongly bonded surface O species. It is not yet certain whether this is O^- or O_2^-. In contrast, AES is effectively incapable of detecting the presence of surface oxygen adsorbed on metallic silver because the photoelectric cross section of the O 1s level for XPS is appreciably larger than the cross section

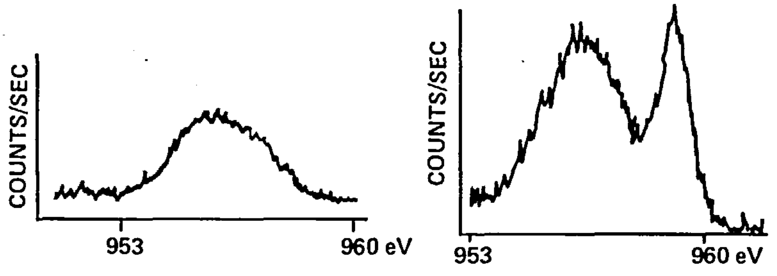


FIGURE 3(a). O 1s signal after exposure of metallic silver to O_2 at 650°K; (b) O 1s signal of silver surface after exposure to excited oxygen at 470°K.

involving K shell-hole Auger transitions. The chemisorption of oxygen on a clean copper surface has also been reported.[47]

A metallic nickel foil was studied by XPS.[48] The Ni 2p electron spectrum was characteristic of a mixture of nickel oxide and metallic nickel. Two oxygen peaks were found. After raising the temperature to 300°C the oxygen signal decreased and there was no oxide structure in the N 2p electron spectrum. After exposure to the atmosphere one oxygen signal appeared from adsorbed oxygen. A theoretical interpretation of XPS oxygen chemisorption on Ni was proposed by Messmer.[54]

The chemisorption of O on Nb, that of CO on Mo and W thin films,[23] that of O_2 on copper and nickel oxides,[49] and of N_2 and NO on W,[50] that of halogeno-alkenes and -alkynes on a Pt (100) surface,[51] and that of H_2, CO, O_2 on noble and transition metals[52] has been reported.

XPS has revealed the first direct evidence of chemisorption of atomic O on (0001) faces of graphite.[54] Brundle and Roberts[22] have reported the sensitivity of XPS for H_2O, CO_2, and CO on gold. Also, the interaction of Hg vapor with gold has been studied, and adsorption and lattice penetration of Hg were observed. In general, less than 10% of a monolayer of H_2O and CO_2 is detectable by XPS, the highest surface sensitivity being reported, so far, as 2×10^{-3} atomic layers.[15] In this case, the ultrahigh vacuum with residual gas pressures below 10^{-8} Pa is a prerequisite for many studies.

d. Alloys

Hulett et al.[56] have used XPS to determine the elemental composition of thin films formed on 70:30 cupronickel exposed to NaCl solutions at different impressed potentials. At anodic potentials below the passivation potential, -0.35 V vs SCE under the experimental conditions, either no film or a film containing Cu and Ni in the same ratio as the alloy existed on the alloy surface. At the passivation potential the spectrum of the passive film indicated primarily nickel oxide and was very similar to the spectrum obtained from a pure Ni specimen passivated in the same environment.

The XPS spectra of PtSn and Pt_3Sn under the influence of heating in vacuo, oxidation, and reduction have been studied.[57] After oxidation the surface is considerably enriched with tin. After reduction the average surface composition is much closer to that of the bulk, but is still richer in tin. These phenomena are reversible.

The effect of doping on the XPS spectra of semiconductors has been studied.[58] Semiconductor XPS line positions are unaffected by changes in the sample's level K fermi level produced by doping. This is due to pinning of the fermi level at the surface by contaminants independent of the bulk fermi level. XPS spectra for the amorphous binary alloys between Ge and Ni and Fe and Au have been studied.[59] The positions and shapes of the main peaks associated with d-band of Ni, Fe, and Au in the spectra change with addition of Ge. The valence orbitals of s and p symmetries of Ge in Ni, Fe, and Au may mix with the s-, p-, and d-orbitals of surrounding host atoms forming bonding and antibonding orbitals.

The low-temperature migration of Si into Au was observed by XPS.[60] This demonstrates the possibility of using the XPS technique to study solid-solid interactions or surface phenomena of solids.

e. Catalysts

The XPS technique as a primary tool in catalysis research has been extensively reviewed.[20] Nitrogen-containing molecules adsorbed on zeolites have been observed, and chemical shifts in the N 1s line of NH_4-Y-zeolites as a function of temperature have been noted. XPS spectra of supported Pt have shown effects of dispersion on the oxidizability of the Pt. XPS spectra of Eu^{3+} exchangeable zeolites and supported Cu and Ni have given evidence of *in situ* reduction after treatment with H_2 at elevated temperatures. Chemical changes in an oxide surface after use as a catalyst have also been reported. Ogilvie et al.[61] have examined a series of copper compounds and catalytic preparations with XPS.

Figure 4 shows the Cu $2p_{3/2}$ lines (right) for a series of preparations. The secondary peaks (left) are due to electrons that are removed from nonground state atoms, either in an excited state or in a doubly-ionized state. These secondary peak positions show the same energy difference from the main peak in each of these spectra. Curve 1 is for $CuAl_2O_4$ and Curve 2 is for CuO. A shift of approximately 1 eV is apparent between the two. Curves 3, 4, and 5 are copper supported on alumina. The binding energy difference between CuO and $CuAl_2O_4$ reveals that more subtle

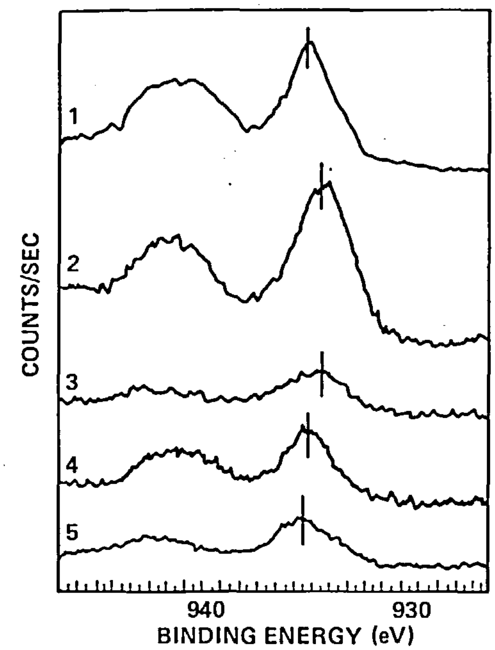


FIGURE 4. Copper $2p_{3/2}$ electron spectra for different preparations with alumina. (Sample numbers refer to Table 2.)

changes than a whole formal oxidation number are being observed. The high surface area alumina (300 m^2/g) impregnated with about 10% copper assumes the $CuAl_2O_4$ structure when calcined at 500°C. The low surface area alumina (75 m^2/g) only forms CuO under the same conditions. After calcination at 900°C, however, it does form $CuAl_2O_4$. The presence of this phase increases physical stability of the catalyst. Escard et al.[62] studied the nature of Ir deposited on alumina as a catalyst in the decomposition of hydrazine with XPS by measuring Ir $4f_{5/2}$ and $4f_{7/2}$ electrons. The existence of electronic interaction is evidenced by the presence of metallic Ir and Ir^{3+} on the surface. Whan et al.[36] reported that XPS spectra for a catalyst prepared by condensing $Mo(CO)_6$ onto γ-alumina show that the Mo in an activated disproportionation catalyst does not exist as hexacarbonyl but is displaced to higher binding energies. The decrease in catalytic activity on exposure of the catalyst to air is believed to be accompanied by oxidation of the Mo.

Okamoto et al.[63] have investigated La_2O_3 - Cr_2O_3 catalysts by measuring the Cr $2p_{3/2}$ electron line. The presence of Cr^{6+} and Cr^{3+} in these catalysts was observed. When the content of chromina is larger, the Cr^{3+} becomes the predominent species.

Tungsten carbide has been proven to be an effective catalyst for many reactions which are readily catalyzed by Pt, but not at all by W. It was speculated that this behavior of W is due to changes in the electron distribution when carbon is added to W. To test this hypothesis, Bennett et al.[168] measured the valence band XPS spectrum of WC and compared it with the spectra of W and Pt indicating that, near the fermi level, the electronic density of states of WC more nearly resembles that of Pt than that of W.

So far we have shown that XPS is indeed a very important tool for studying catalysis. Since there are a great number of catalysts and catalysis is a complicated phenomenon, not all catalytic problems can be easily solved by UPS or XPS, which has its limitations. For instances, Armour et al.[35] have reported binding energies for molybdenum(VI), cobalt(II), and iron(III) in ammonium di- and hepta-molybdates, cobalt(II), and iron(III) molybdates, and fresh and sulfided cobalt-molybdenum-alumina (CMA) catalysts. There were

TABLE 2

XPS Binding Energy and K-Absorption Edge Shifts

Sample				Shift of binding energy from Cu° value (eV)	Shift of K-absorption edge from Cu° value (eV)
No.	Copper (wt %)	Supporting surface area (m^2/g)	Calcination temp (°C)		
1	$CuAl_2O_4$	–	–	3.20	7.94
2	CuO	–	–	2.25	3.86
3	10.3	72	500	2.35	4.50
4	10.3	72	900	3.10	7.73
5	8.8	301	500	3.30	7.73

no features of the spectra which could be attributed to Mo and Co in different structural environments. Structural changes occurring when Fe(III) molybdate is calcined were not observed in XPS spectra. Mo binding energies were particularly high in CMA catalysts, indicating a high effective positive charge of Mo. Mo and Co binding energies were lowered after sulfiding CMA catalysts.

f. Coatings

During the course of studies on the use of electrical discharge treatment to graft organic monomers on the surface of wool fibers, Millard and Pavlath[64,65] explored the use of XPS for detecting coatings and chemical changes on the surface of wool fibers. Organic coatings containing F, P, and Si were detected on the surface of fibers. S atoms on the surface were oxidized to S^{6+} state by these treatments.

The XPS spectra of five types of polyacrylonitrile-based fibers were examined.[66] An appreciable increase in oxygen bound to the surface after oxidation was observed. There were two distinct kinds of carbon atoms in oxidized Courtelle carbon fiber. Kim et al.[67] have reported the direct spectral observation of chemisorbed oxygen on a Pt surface and binding energies for oxides produced from chemical oxidation of the Pt substrate. Although the spectral measurements cannot be performed in the electrochemical cell, the unequivocal chemical identification of electrochemically formed surface compounds would aid tremendously in interpreting the corresponding current-potential behavior. They observed the presence of discrete stoichiometric platinum oxides on the electrode surface and considered this to be the most definite spectroscopic evidence yet available that would confirm their existence. Comparison of XPS data to other results, especially low-energy electron diffraction data, may further aid in understanding chemisorption and coatings.

Photoelectron spectroscopic investigations of thin gold films evaporated onto glass have been made by Ebel and Ebel[68] in order to find the attenuation coefficients for electrons in solids; these are of value in quantitative analysis. The effects of "density defects" and lack of electrical conductivity have been discussed in detail. An encompassing and exact knowledge of photoelectron attenuation coefficients for different electron energies in different elements is the basis for a theoretically grounded quantitative analysis of metallic bonds. Such an analysis can only be realized with consideration of all the sources of error.

g. Corrosion

XPS is a surface technique which is useful in the study of corrosion. Examination of lead-indium and lead-tin alloys by XPS has provided an insight into the way in which these materials resist corrosion. The tin and indium are found to be markedly segregated at the surfaces and in the oxidized form. The alloying elements additionally help the formation of a state of lead more highly oxidized than that found on the surface of pure lead under the same conditions. The corrosion-resistance of the alloys increases progressively with concentration of alloying elements, and the amounts of lead oxide observed decline with increasing indium or tin content. The behavior of the protective alloying elements is not quite straightforward, in that they seem to be more readily oxidized than when pure. They promote the lead to a higher oxidation state, like PbO_2 rather than PbO, which occurs on pure lead.

Reactions of evaporated iron with oxygen and water have been investigated by Kishi and Ikeda.[75] The Fe $2p_{3/2}$ and O 1s electron lines were measured during the course of reactions, and their variation was discussed, by the authors, in terms of the positive and negative charges of the Fe and O (in the surface oxide formed), respectively, assuming a simple charge-chemical shift relation. High reactivity of the surface oxide with water and the resulting hydroxyl group formation was observed. An approximate estimate of the Fe to O atomic ratio of the surface oxide was also carried out based on the Fe and O peak areas. Kishi and Ikeda[71] also carried out a similar experiment on evaporated nickel exposed to oxygen and water. The Ni $2p_{3/2}$ and O 1s electrons were measured by XPS technique during the interaction of the evaporated Ni with oxygen and water. Two kinds of peaks were observed for both Ni and O in the surface species. In the reaction of the surface species with water an electron transfer was noted.

Fischmeister and Olefjord[44] have applied XPS technique to the analysis of the thinnest oxide layers, such as those responsible for the passivity of stainless steel. They studied the primary oxide layer formed at room temperature on steels of the type Fe 18 Cr 10 Ni. The oxide layer contained mainly Fe^{2+} and Fe^{3+}; Cr or Ni could also be detected. The XPS spectra of iron in various oxidation states are shown in Figure 5.

h. Angular Distribution of Photoelectron Spectra

Measurements of the photoelectron spectra of molecules as a function of angular θ between the direction of the incident photon and that of the outgoing photoelectron offer excellent supplementary information by which the nature of the molecular orbital corresponding to a given photoelectron peak may be determined. A number of such angular studies have been made in the past on molecules.[72,80]

For a dipole transition involving an unpolarized beam of photons and randomly oriented molecules, the intensity for a given photoelectron peak is[73,75]

$$I(\theta) \propto 1 + 0.5\beta(3/2 \sin^2 \theta - 1) \qquad (1)$$

where the angular parameter β depends on the

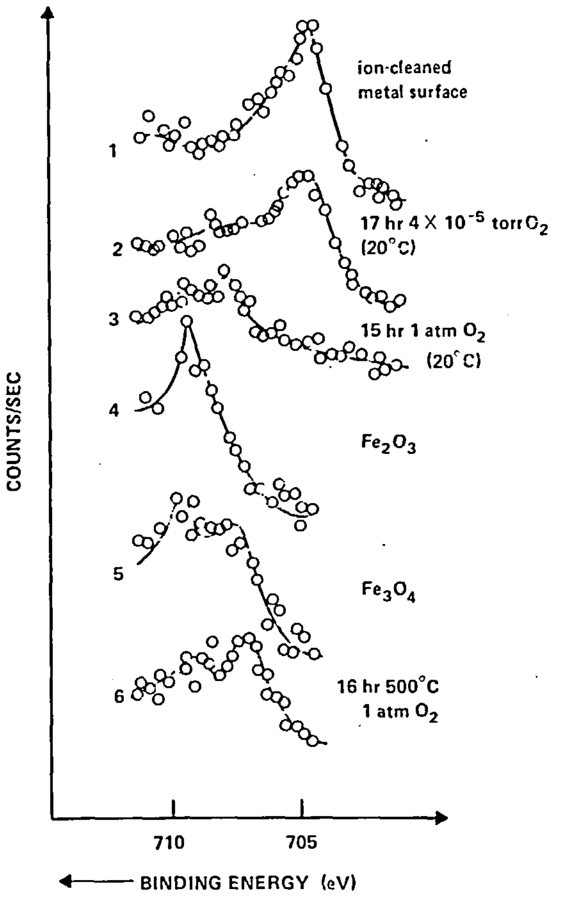


FIGURE 5. XPS spectra of Fe (L_{III}) in different states.

photon energy and the nature of the molecular orbital from which the photoelectron is ejected. The values for β may range from -1 to $+2$. The β parameter characterizes the angular distribution.

Fraser et al.[81] found that in an ultrahigh vacuum the surface sensitivity (ratio of surface to volume signal) of the technique to be enhanced by approximately one order of magnitude at low angles of electron emission measured from the surface plane (θ'). The Mo $3d_{5/2}$ electron line intensity from a clean polycrystalline Mo surface was independent of angle in the range $25° < \theta' < 65°$; however, the Cs $3d_{5/2}$ electron line intensity from an adsorbed Cs layer on Mo increased, and the Mo $3d_{5/2}$ signal from the Mo substrate decreased as the angle of emission was decreased. It is proposed that the angular dependence of spectral intensities can be used to differentiate surface from bulk species.

Fadley et al.[82] presented an excellent study of the theoretical and experimental applications of XPS angular distribution measurements to quantitative surface characterizations. The authors discussed the basic theoretical model that has been used in the past to analyze the angular distributions from flat surfaces in the absence of electron-diffraction (channeling) effects, including certain new generalizations and special cases pertinent to surface analysis. The applications of this model are in agreement with new experimental results obtained from gold samples with carbon-containing surface layers and from aluminum samples with successive oxide- and carbon-containing layers. An order of magnitude increase in surface-layer relative intensities was also observed at low electron ejecting angles relative to the surface. This confirms the findings of Fraser et al.[81]

Also, the effects of X-ray refraction and reflection were found for very low angles of photon beam incidence, and these lead to approximately a four-fold increase in surface-layer relative intensities. Rough surface intensities will equal flat-surface intensities provided that both surfaces are clean and that no X-ray shading occurs. When surface layers are present, rough-surface angular distributions are predicted to deviate markedly from flat-surface distributions. The authors concluded that it may be possible, with angular distribution measurements, to selectively enhance near-surface contributions to photoelectron spectra, as well as to gain information about electron mean free paths, uniformity, surface layer thickness, and even surface roughness.

i. Clean Surfaces

Sample preparation is of utmost importance in any chemical analysis. It is particularly true for surface analyses, as one can encounter clean as well as "dirty" surfaces. For an accurate surface analysis, both ultrahigh vacuum and clean surface are necessary. At pressures of 10^{-10} torr, surfaces may be maintained for a period of hours before being covered by a monolayer of contamination. Many instruments are equipped with sample treatment accessories for bombardment cleaning of surfaces contaminated by exposure to gaseous atmosphere or vapor deposition. Most XPS instruments are operated in the 10^{-7} torr range. The sensitivity is 1% of sampled volume. Useable signals are obtained from 0.1 to 10 monolayers or 10^{-6} to 10^{-9} g of surface material.

In the early years the investigators cleaned the oxide contamination of surface by treatment with H_2 at an elevated temperature. In recent years the sputtering technique has been applied to cleaning surfaces of UPS and XPS work. For instance, the argon ion gun for cleaning surfaces has been described.[83] Some commercial XPS instruments are equipped with an ion gun.

For precise surface research, a clean surface has been emphasized.[16,17,85] Ranke and Jacobs[84] stated that photoelectron spectra from the clean polar (111) and ($\overline{1}\overline{1}\overline{1}$) faces of GaAs show emission from surface states. After a brief exposure to oxygen which produces a coverage of approximately one monolayer, this emission disappears. Brundle and Roberts[22] have compared the UPS spectrum of clean Au surface and that of Au surface contaminated with C and F (Figure 6).

Solar-wind sputtering has been proposed as one of the possible mechanisms for producing darkening of the lunar surface. In the process of sputtering, oxygen, owing to its high sputtering yield and high volatility, is more likely to escape from the surface than the heavy metal atoms. Consequently, the bombarded surface undergoes gradual chemical reduction that is probably nonstoichiometrical. For instance, in a sample containing iron oxides it is possible to reduce Fe^{3+} first to Fe^{2+} and eventually to Fe^0 under prolonged ion bombardment. Yin et al.[102] studied the possible solar-wind darkening of the lunar surface by XPS. The samples of Fe_2O_3, Fe_3O_4, FeO, and Fe foil showed that chemical reduction does take place on the sample surface when Ar ion bombardment occurs. After prolonged bombardment the surface of all four samples consisted predominently of Fe^0 in the metallic state (dark). Argon ion sputtering of 15 silicate and oxide samples under similar conditions produced surface darkening only in the samples containing iron.

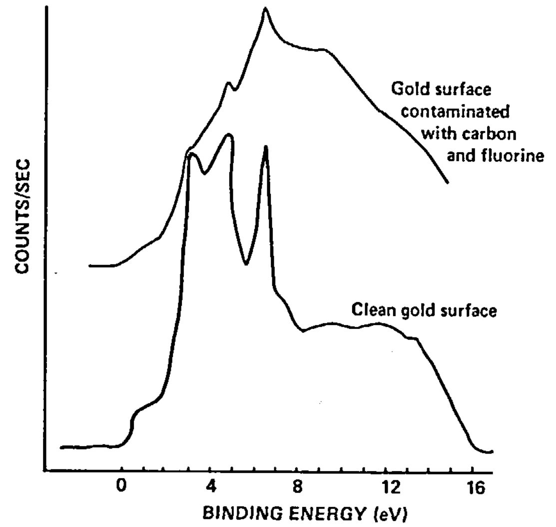


FIGURE 6. He(I) spectrum of clean gold (lower trace) and carbon- and fluorine-contaminated gold (upper trace).

Many problems remain to be solved in the cleaning of surfaces with ion bombardment or sputtering. The treatment should be just right to remove the dirty layers without changing the real surface of the sample. The ion gun bombardment is a process of physical chemical itching producing a hole. Care should be taken when the ion bombardment is employed to clean the surface without disturbing the surface to be examined.

B. Bulk Analysis

In an attempt to make XPS quantitative, many aspects of the technique have been studied. The first quantitative experiments were reported in 1951 by Steinhardt and Serfass,[3] in which analyses of gold-silver alloys were made along with analyses of brass and some pure metals. An error of 4% for the gold-silver analysis was said to be encouraging in view of the resolution obtained in the work.

It was quite some time until Nordling et al.[86] improved the technique and showed the necessity of certain corrections on the intensity of photoelectron lines in order to make the results quantitative. The corrections were for: (a) Z-dependence of photoelectric cross section, (b) attenuation of the photoelectrons leaving an irradiated surface, and (c) detection efficiency. Since these preliminary experiments, the factors influencing the intensity of photoelectron lines have been studied in detail and will be discussed in this section.

Wagner[87] summarizes the four main factors influencing the line intensity as: (a) photon flux; (b) cross section for electron-photon interaction; (c) space-intergrated escape probability, without loss of energy-inelastic scattering cross section; and (d) sensitivity of detection of electrons by a given instrument. By referencing all line intensities to that of the F 1s or Na 1s line intensity and thus determining relative intensity, he obviated the need for considering the effects of variations in photon flux with time. This use of an internal standard for intensities would appear to be necessary in the absence of a very stable X-ray flux.

The subject of photoelectron absorption cross sections has been studied by several groups[87–91] and was found to be dependent on three factors. The first was a Z^4-dependence that favors elements of high atomic number. Secondly, a dependence on binding energy was found to exist that causes the cross section to rise rapidly as the binding energy approached the energy of the incident photons. Lastly, the cross section was shown to have a strong dependence on the angular momentum quantum number for photons in the energy range used in XPS. Taking into account the above factors, one can explain the periodicity of the intensities of the lines arising from elements 3 to 92 as shown in Figure 7.

The escape probability of photoelectrons from the solid surface, without energy loss, has been shown to be directly proportional to the kinetic energy of the photoelectron.[87] This would, of course, make the intensity a function of the energy of the incident photon and the binding energy of the electrons giving rise to the line. The factors above would appear to favor elements with a low atomic number for a given value of a principal quantum number.

Two factors that influence the ability of a photoelectron to escape the solid surface are surface roughness and extent of contamination. These two factors have been rigorously dealt with by Ebel et al.[92] In this article the authors drew upon mathematical treatments that have had success in X-ray fluorescence analysis, in an attempt to correct XPS intensity for surface roughness. It was found that a certain amount of the surface is "shadowed" from the incident photons, and this amount increases with roughness of the surface. The amount of attenuation due to this effect is proportional to the diagonal of the "cube" face, with values $> 10^{-6}$ cm giving a noticeable decrease in intensity and values $> 10^{-4}$ cm being quite detrimental to accurate quantitative experiments. The authors concluded that XPS samples should be polished with fine abrasives (in the case of metals and alloys) or pressed into

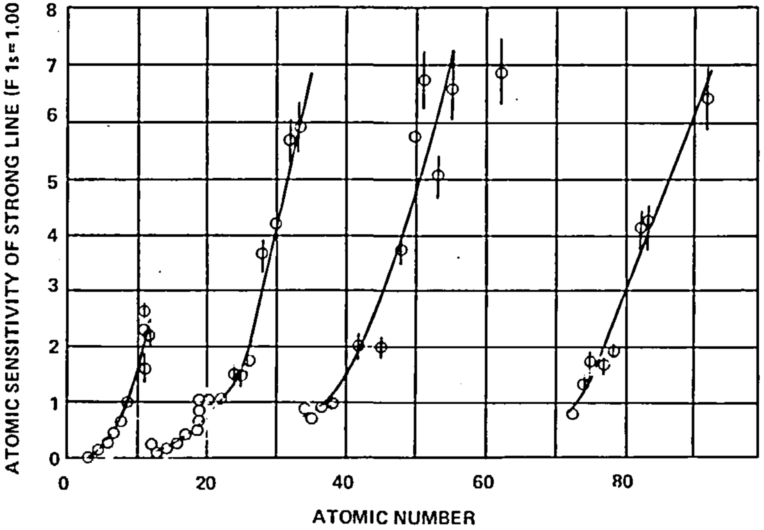


FIGURE 7. Atomic sensitivity of the elements. (From Wagner, C. D., *Anal. Chem.*, 44, 1050 (1972). Copyright by the American Chemical Society. With permission.)

plates (in the case of powders) in order to regulate the effects of surface roughness.

Contamination on the sample surface usually stems from a variety of sources and cannot be treated theoretically on a general basis. In the case of many surfaces vacuums on the order of $< 10^{-10}$ torr and ion etching of the surface by bombardment with argon ions have been shown to help in maintaining a clean surface (see section on surface analysis).

The last major factor determining peak height is the efficiency of detection of the photoelectrons. There are several influences on this efficiency: solid angle of acceptance of electrons into the analyzer, transmission function of the analyzer, and type of detector used. It is beyond the scope of this section to discuss these factors in detail, but it should be noted that for a given spectrometer these influences should be constant and may be corrected for in the spectra. A detailed method for determining transmission function has been given by Poole et al.[93] The authors described the intensity vs kinetic energy corrections in UV work.

Measurement of intensity and half width have various theoretical applications,[88] but quantitative analysis is of the most interest to analytical chemistry. With all the above factors controlling the intensity of XPS lines, it is of major interest to review the successes that have been obtained with the technique.

Reviewing the work in a loose chronological order, one starts with the experiments done in 1964 by Nordling et al.[86] and given in more detail in a book by Siegbahn.[7] In these experiments the XPS spectra of a variety of inorganic and organic compounds were recorded, attention being focused on chemical shifts and intensity of the lines arising from the various constituent elements.

With respect to analysis of inorganic alloys, some very good results were obtained. The relative amounts of copper and zinc in five samples of varying composition were examined in their study.[7] Using one of the samples as a standard, the other four were analyzed with about 2% accuracy. Another sample of brass containing 0.68% tin and 0.82% lead was also run. The small amount of the two metals was easily detectable. Figure 8 gives the results of this experiment. Another fine example in this work was the analysis of insulin and five amino acids by XPS where elemental ratios were obtained that agree quite well with the calculated values based on the empirical formulas (Figure 9 and Table 3).

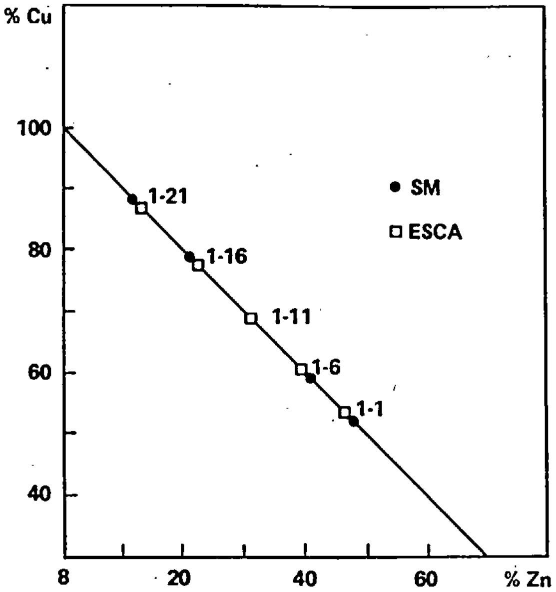


FIGURE 8. The relative amount of copper and zinc in some brass alloys as measured by ESCA. The results are compared with data (SM) given by the factory, Svenska Metallverken. (From Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Heden, P. F., Hamrin, K., Gelius, U., Bergmark, T., Werme, L. O., Maume, R., and Baer, Y., *ESCA Applied to Free Molecules*, North-Holland, Amsterdam, 1969, 148. With permission.)

From this work the authors made the following conclusions: (a) heavy and light elements may all be studied alike; (b) the absolute sensitivity is high (i.e., the amount necessary for analysis is on the order of 10^{-8} g); (c) the technique, for the most part, is nondestructive; (d) amorphous as well as crystalline samples may be studied; and (e) the chemical shifts may be used to quantitatively determine oxidation states of metals and organic functional groups.

This basic work was followed in time by a study on solutes undertaken by Kramer and Klein.[94] In this work varying amounts of $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$ dissolved in aqueous solutions were frozen and XPS spectra were taken. A direct linear correspondence between molar concentration and XPS peak intensity for Fe 3p core level was found. The work covered the concentration range between 0.05 and 1 *M*, with a constant concentration of sodium chloride (1 *M*) used as an internal standard.

A few problems involving nonuniformities of concentration evolved from the freezing process.

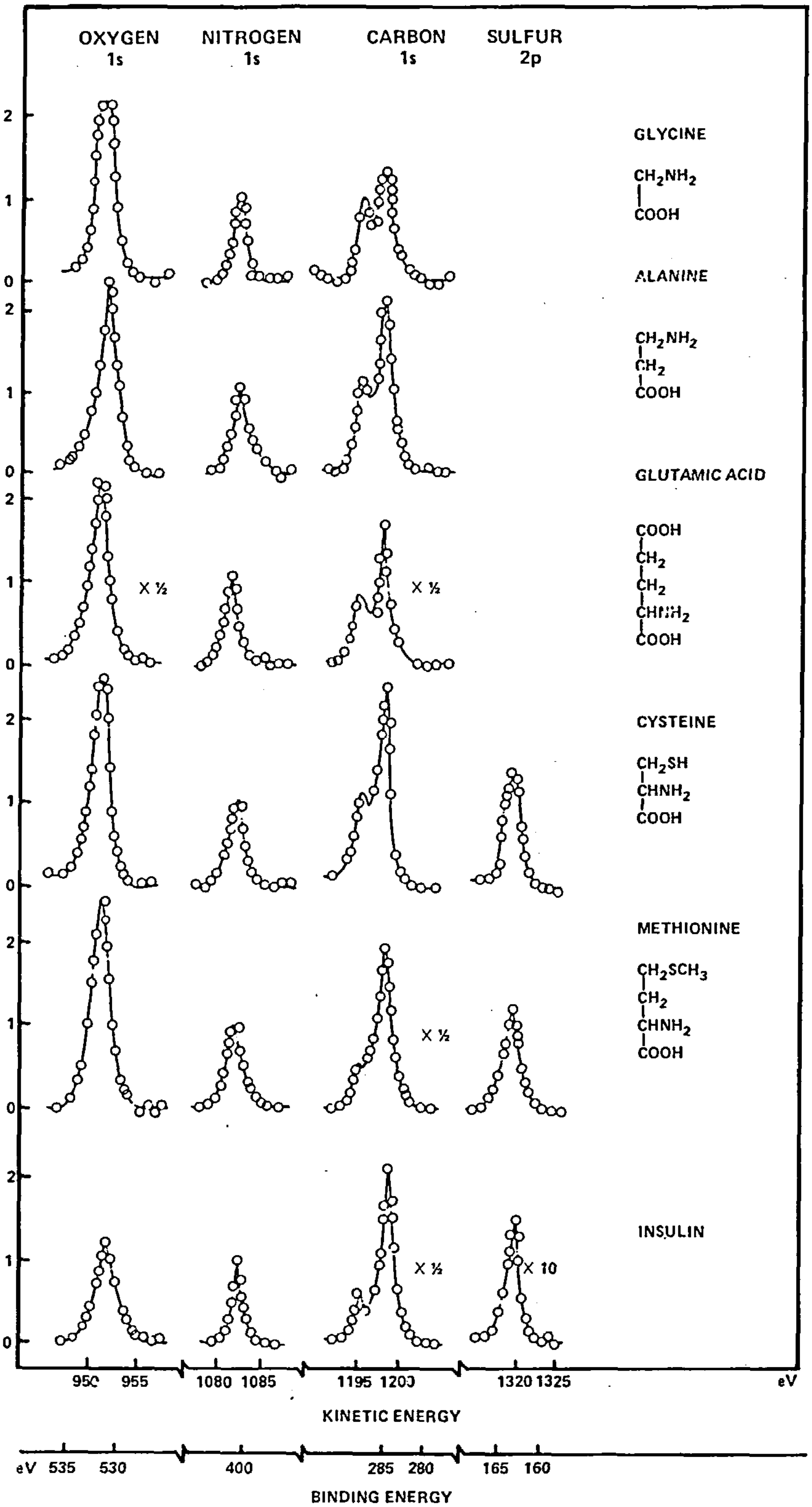


FIGURE 9. Electron spectra from five amino acids and from insulin. The lines are related to the nitrogen 1s line as unity. (From Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Heden, P. F., Hamrin, K., Gelius, U., Bergmark, T., Werme, L. O., Maume, R., and Baer, Y., *ESCA Applied to Free Molecules*, North-Holland, Amsterdam, 1969, 47. With permission.)

TABLE 3

Elemental Analysis of Insulin and Five Amino Acids by ESCA

Compound		Observed relative amounts					
Name	Empirical formula	C_O	C_H	C	N	O	S
Glycine	$CO_1CH_1H_5NO_2$	1	1	2	1	2	0
Alanine	$CO_1CH_2H_7NO_2$	0.99	1.95	2.94	1	1.87	0
Glutamic acid	$CO_2CH_3H_9NO_4$	1.96	3.05	5.01	1	3.60	0
Cysteine	$CO_1CH_3H_7NO_2S$	0.97	2.02	2.99	1	1.90	1
Methionine	$CO_1CH_4H_{11}NO_2S$	0.99	3.98	4.97	1	1.90	0.87
Insulin	$CO_{61}CH_{193}H_{450}N_{65}O_{75}S_6$	61	205	271	65	66	5.7

(From Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Heden, P. F., Hamrin, K., Gelius, U., Bergmark T., Werme, L. O., Maume, R, and Baer, Y., *ESCA Applied to Free Molecules*, North-Holland, Amsterdam, 1969, 144. With permission.)

To eliminate this problem addition of methanol and subsequent glass formation on quick freezing in liquid nitrogen was tried, but more comprehensive experimentation was suggested. The results were good and it seems that there are many applications in areas where it is impossible to isolate certain species from solution or in investigations of kinetic rates and reaction mechanism. The technique does necessitate the use of sophisticated sample handling and a low-temperature probe that can keep the sample frozen while data is taken.

Another quantitative application of XPS is seen in the complementary data obtained by Davis et al.[95] and Davis[96,97] on "polywater" and "polyheavy water." Several techniques, including infrared and spark source mass spectrometry among others, were used to investigate this substance in 1970 to 1971. The results given by Davis et al.[95], done in two independent laboratories, gave qualitative results that were not only consistent with the other techniques but also gave insight into the actual forms that the constituent species were existing as in "polywater." In all, some 11 different species were definitely identified and a semiquantitative idea of the relative amount of each was obtained.

As is well known, it was found that the anomalous water and heavy water contained very little hydrogen or deuterium. The experiments did, however, demonstrate the ability of XPS to give a detailed semiquantitative elemental analysis of a compound of completely unknown composition.

Two quite similar articles by Klein and Kramer[98,99] appeared in 1970 to 1971 as proceedings of symposia and dealt with a very practical problem of protein analysis in seeds. In these studies a relatively simplistic approach to extraction of quantitative data from XPS spectra was taken with, however, fairly good results when compared to other methods of analysis (Table 4a, b, and c). The main thrust of the work was to arrive at some quick method for screening seeds from various sources as to their total protein content and the quality of the protein that was present. Not only was total protein measured as a function of the N 1s line intensity, but free amino nitrogen was found to be a measure of lysine, arginine, and histidine, and the sulfur line a measure of cysteine, cystine, and methionine.

In an effort to better understand what could be expected, many pure samples were run. It was found that amide and amino nitrogen could be distinguished. Table 4a shows the reproducibility of the technique for independent samples. For the seeds, a cysteine sample mixed with sodium chloride was used to determine spectrometer factors and set up a calibration procedure. The seeds were then analyzed. The experimental weight percentage of nitrogen, determined from the XPS amide nitrogen peak, was converted to percentage protein by assuming a nitrogen:protein weight ratio of 0.15.

The technique proved to be fairly rapid and useful for quantitative work. It was stated that with improvements in the instrument to decrease data acquisition time, the process would be feasible for large screening of seeds. It should also be noted that the procedure was nondestructive in that seeds that were analyzed only for total protein content (the embryo not being disturbed) could still be brought to germination. Millard and

TABLE 4a

Quantitative Determination of Nitrogen and Sulfur Content

Compound	Element	Experimental weight (%)	Calculated weight (%)
Cysteine* (1)	Nitrogen	8.2	8.2
	Sulfur	18.0	19.3
Cysteine* (2)	Nitrogen	8.5	8.5
	Sulfur	20.0	19.3
Cystine (1)	Nitrogen	13.0	11.7
	Sulfur	26.3	26.7

*Cysteine-hydrochloride-monohydrate.

TABLE 4b

Elemental Analysis

Seed	% N(XPS)	% N(anal)	% S(XPS)	% S(anal)
Barker barley	1.5 ± 0.2	1.5 ± 0.2	0.05 ± 0.02	0.01 ± 0.01
Ramona wheat	1.6 ± 0.2	1.7 ± 0.2	0.05 ± 0.02	0.06 ± 0.03
Rapida oats	2.2 ± 0.2	1.9 ± 0.2	0.1 ± 0.03	0.02 ± 0.02
Light red kidney bean	3.2 ± 0.3	4.1 ± 0.3	0.08 ± 0.04	0.13 ± 0.06

TABLE 4c

Seed Protein Distribution (Light Red Kidney Bean)

Sample	% N(XPS)	% N(anal)	% Basic AA (XPS)	% Basic AA(anal)
Endoplasm	3.1 ± 0.3	4.0 ± 0.3	17 ± 5	
Embryo and endoplasm			17.4	17.4
	3.1 ± 0.3	4.2 ± 0.3	18 ± 5	

(From Klein, M. P. and Kramer, L. N., in *Symposium: Seed Proteins,* Proc. ACS Meet., Los Angeles, California, 1971, Inglett, G. E., Ed., Avi Publishing, Westport, Conn., 1972, 265. With permission.)

Masri reported the analysis of modified proteins by XPS and stated that when specific reagents, such as F and Hg, for protein modification are used, the XPS technique is most accurate to estimate the functional group content of the protein.[170]

Vinogradov et al.[100] and Nefedov et al.[101] have used the XPS technique in many qualitative and quantitative studies of minerals from various parts of the world and space. One of the more interesting works is being done on lunar regolith and meteorite samples.[100,101] By running the total XPS spectra, the authors were able to determine the composition of the lunar samples. Table 5 gives a comparison between these and earth samples of similar materials.

Several interesting results arose from the lunar samples, one being that the coordination number of aluminum atoms in the lunar samples is four, as seen in a shift of 2.3 eV from metallic aluminum. These results lead to the conclusion that extreme acid and base mineral phases are not present in essential amounts in lunar regoliths. The most interesting results, however, come from a comparison of the Fe 2p lines in lunar and earth samples. In all the lunar samples there are lines from

TABLE 5

The Compositions of Lunar Regoliths, Eucrite and Oceanic Gabbro (wt %)

Component	The regolith from the Sea of Fertility Luna-16-A3	The regolith from the Sea of Tranquility 10005,35,2	Eucrite chervony koot (Chirvinsky, Sokolova, 1946)	Oceanic gabbro
SiO_2	42	43	49	27
Al_2O_3	15	13	13	12
Fe_2O_3	–	–	–	14
FeO	17	16	19	17
MgO	12	12	11	5
CaO	8.7	8	7	10
TiO_2	3.4	7	0.7	8
Na_2O	0.4	0.5	0.5	0.6
K_2O	0.1	0.1	0.1	0.9
S	0.2	–	–	–
Ni	0.02	0.007	–	–

(From Vinogradov, A. P., Nefedov, V. I., Urosov, V. S., and Zhavoronkov, N. M., Proc. 3rd Lunar Science Conf., MIT, Cambridge, 1972, 1422.)

metallic iron which are absent in the terrestrial samples (Figure 10). Similar results were obtained by Yin, et al.[102] From the XPS data it appears that this metallic iron constitutes 10% of the total iron. Results from Mossbauer and ESR[100] experiments, however, show the concentration to be in the 2 to 5% range. This brings up a point that must always be considered in bulk analysis of only a thin portion of the surface. Extreme precautions must be taken to insure homogeneity of the sample. Of course, this problem can be used to an advantage, as in the case of the lunar samples, by making use of the data to obtain information about where certain species exist in a sample.

The Fe 2p lines from the meteorites also showed traces of metallic iron, but unlike the lunar samples, the intensities of these lines sharply decreased on exposure to air. This lead Vinogradov et al.[100] to the following conclusions: (a) the metallic iron from the lunar samples is of high purity (or an unusual set of dopants is present); (b) condensation of the metallic phase under very high vacuum leads to the above characteristics; and (c) irradiation by solar wind (ionic flow) for a long time has some special effect on the iron surface.

The analysis of mixtures of MoO_3 and MoO_2 by XPS given by Swartz and Hercules[103] was the first report of an instrumental technique capable of such analysis. Other analytical methods which were able to give total molybdenum content were not able to distinguish between the existing oxidation states of the molybdenum and the wet chemistry techniques and were too time-consuming for rapid analysis.

By studying a series of molybdenum compounds in varying oxidation states the authors[103] demonstrated the point that both Mo $3d_{5/2}$ and Mo $3d_{3/2}$ peaks were shifted equally by a given change in oxidation state and were separated by 3.0 ± 0.2 eV. A shift in binding energy of the Mo 3d lines of 1.7 eV was found on going from MoO_2 to MoO_3. This magnitude of shift allowed XPS to distinguish between MoO_3 and MoO_2 in mixtures of the two (Figure 11). The necessary calibration curve was derived by measuring the (counts E)/Counts (E + 4.7 eV) ratios for a series of synthetic mixtures (Figure 12). The mixture was prepared by weighing given amounts of each oxide and throughly mixing with mortar and pestle. These mixtures contained from 5 to 95% MoO_2. The procedure was then checked by the preparation of mixtures of various concentrations, unknown to the authors, by another investigator. These results are given in Table 6. The time required for analysis of a mixture was about ½ hr, but it was postulated that this could be cut in half, and at worst only 45 min would be necessary for extreme cases of concentration.

This work represents the first analysis by XPS that is not possible by another technique. The authors foresee extension of the above procedure to analysis of other oxide pairs (i.e., PbO – PbO_2,

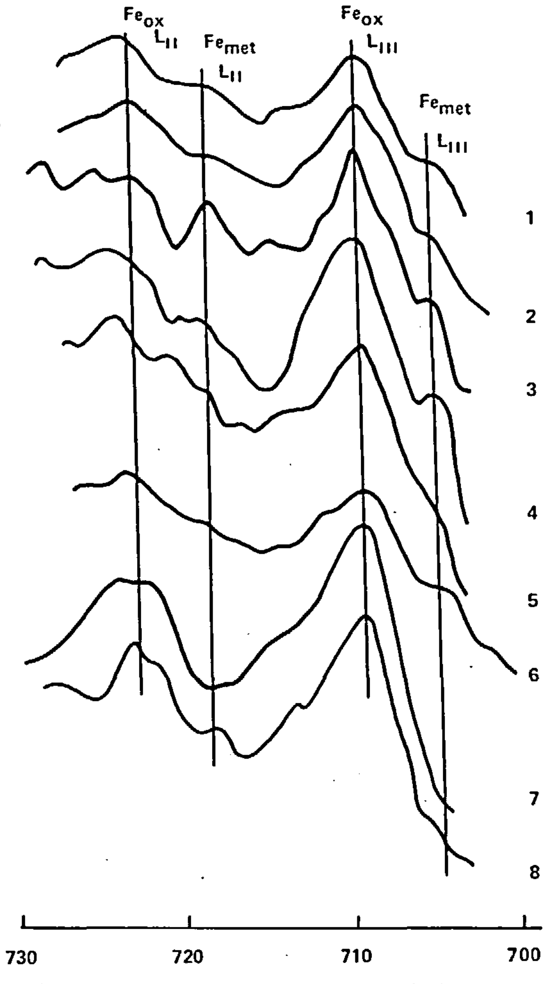


FIGURE 10. Fe 2p lines. (1, 2) The regolith from the Sea of Tranquility; (3 to 6) The regolith from the Sea of Fertility; (7) Oceanic gabbro; (8) Eucrite Chervony Koot. (From Vinogradov, A. P., Nefedov, V. I., Urosov, V. S., and Zhavoronkov, N. M., Proc. 3rd Lunar Science Conf., MIT, Cambridge, 1972, 1423.)

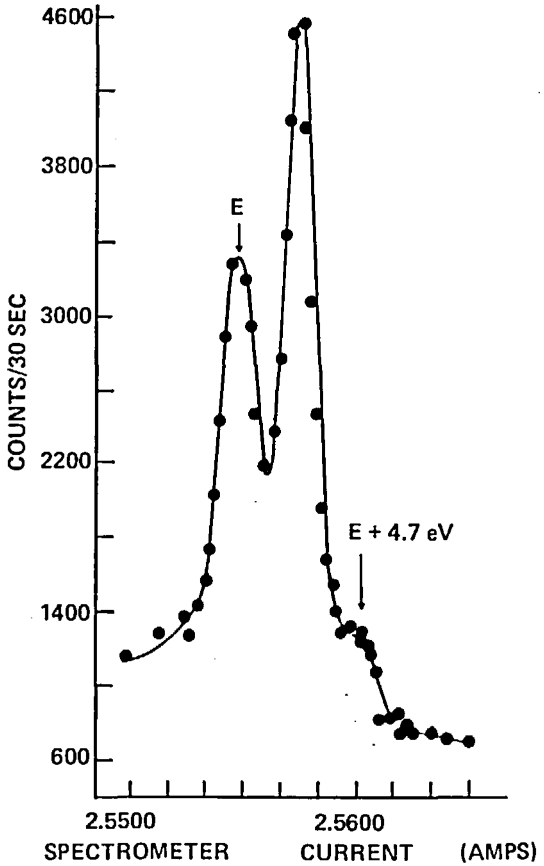


FIGURE 11. Molybdenum (3d$_{3/2}$ to 3d$_{5/2}$) electron spectrum for a 27:75 (MoO_3-MoO_2) mixture. (From Swartz, W. E., Jr. and Hercules, D. M., *Anal. Chem.*, 43, 1777 (1972). Copyright by the American Chemical Society. With permission.)

Cr_2O_3 – CrO_3, As_2O_3 – As_2O_5, and possibly WO_2 – WO_3. The applicability of this technique is dependent on the magnitude of the shifts in binding energy between the adjacent oxidation states in the oxide pair and the stability of the -ous species to further oxidation under the experimental conditions.

Larson[104] submitted a report of a quantitative investigation of the intensity of XPS lines as a function of composition in gold-silver alloys of varying but accurately known composition. The results of the experiment yielded a straight-line correlation among intensity and content for

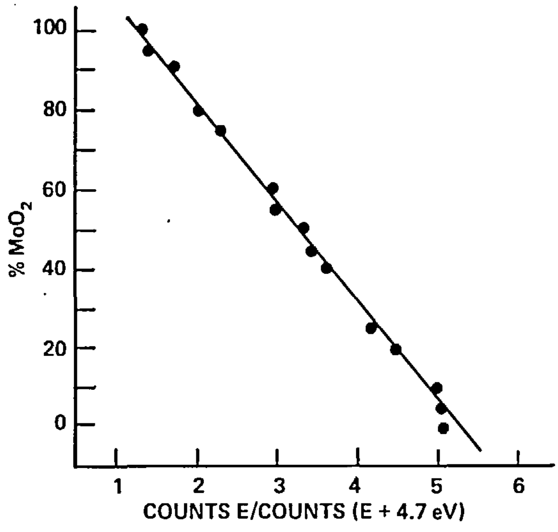


FIGURE 12. Calibration curve for quantitative analysis of MoO_3-MoO_2 mixtures. (From Swartz, W. E., Jr. and Hercules, D. M., *Anal. Chem.*, 43, 1778 (1971). Copyright by the American Chemical Society. With permission.)

TABLE 6

Percentage of MoO_2 Determined for Unknown Mixtures of MoO_2 and MoO_3

Unknown	MoO_2 %	MoO_2 determined, %
A	51	53 ± 1
B	46	52 ± 6
C	47	50 ± 3
D	80	82 ± 2
E	20	23 ± 2

(From Swartz, W. E., Jr. and Hercules, D. M., *Anal. Chem.*, 43, 1778 (1971). Copyright by the American Chemical Society. With permission.)

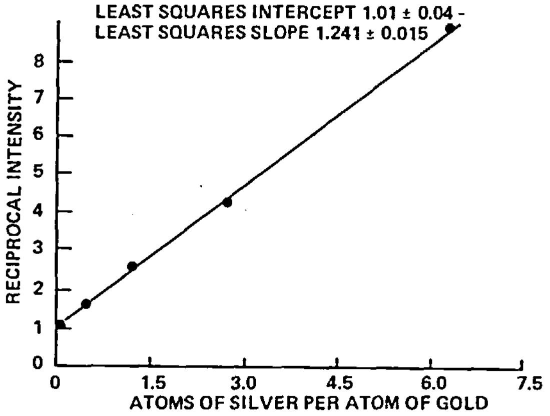


FIGURE 13. Composition dependence of photoelectron line intensity. The straight line is a least-squares approximation to the experimental data. (From Larson, P. E., *Anal. Chem.*, 44, 1680 (1972). Copyright by the American Chemical Society. With permission.)

samples as reflected by a plot of reciprocal intensity of the Au $4f_{7/2}$ line vs. Ag atoms/Au atoms in the 0 to 100% gold range (Figure 13 and Table 7). Moreover, the author was able to calculate from the data a relative total inelastic cross section for 1,165-eV electrons escaping from the solid samples. By suitable choice of other photon sources and/or other photoelectron lines one could gain more information about inelastic scattering of electrons of other energies.

The latest applications of XPS to analysis of bulk concentration, dealing with analysis of polymeric compounds, have been carried out by Clark et al.[105,106] and Phillips.[107] Clark et al.[105,106] did not use the XPS data to determine absolute amounts of atoms in the compounds, but instead determined relative amounts of functional groups as represented by varying oxidation states of carbon and nitrogen in nitroso rubbers. The results agreed with estimates made by other means.

Phillips[107] used the same technique to characterize fluoroalkyl polymethacrylate homopolymers and segmented fluoroalkyl carboxylic acids of the type $F(CF_2)_n$-$(CH_2)_mCOOH$. Several factors were found to influence the line intensity and thus the F/C and O/C ratios. Surface roughness caused variation in the intensities, as was discussed above for samples of varying particle size in succinic and maleic acids. This gave approximately a one third decrease in C 1s signal for an approximately 75% increase in particle diameter.

It was also found that choice of standards was very critical, influenced by the similarity of the standard and unknown with respect not to composition but to side chain orientation and matrix parameters. That is, a long chain perfluoro carboxylic acid, as shown in Figure 14, will give rise to different F/O ratios, depending on whether the CF_3 end or the COOH end of the molecule is at the surface. Molecular orientation is, therefore, important when trying to relate experimental atomic ratios to stoichiometry.

TABLE 7

Analysis of Au 4f Photoelectron Intensity Data According to Sample Composition

Au, %	$\eta Ag/\eta Au$	Relative integrated intensity	Diameter, inch	Corrected intensity	Reciprocal intensity
100	0	7.95	0.0182	8.74	1
80	0.455	4.84	0.0181	5.34	1.64
60	1.21	2.96	0.0173	3.42	2.56
40	2.73	1.96	0.0191	2.05	4.26
20	6.32	9.93	0.0190	0.98	8.92

(From Larson, P. E., *Anal. Chem.*, 44, 1680 (1972). Copyright by the American Chemical Society. With permission.)

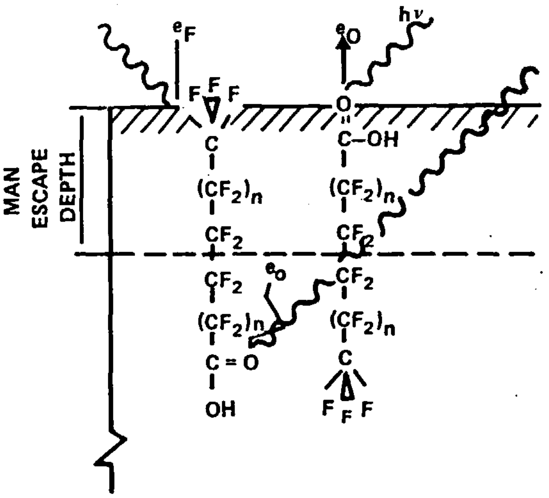


FIGURE 14. Schematic showing orientation effects in X-ray photoelectron spectroscopy. (From Phillips, R. W., *J. Colloid Interface Sci.*, 47, 694 (1974). With permission.)

Other factors that must be considered are decomposition by X-radiation and surface contamination by hydrocarbons. Time of X-radiation was found to influence the intensity of the spectral lines, but by what mechanism is unclear. The effect could result from simple decomposition or from the X-ray induced electronic emission causing charged surface-active species to enhance the contamination rate. In any event, Figure 15 shows the variation of intensity vs. time of X-ray exposure. This type of decomposition by X-rays is a point very often overlooked and, in light of the high-intensity X-ray flux of commercial X-ray tubes, one that should receive much attention. Two other papers that make mention of this problem show that a change in the spectra can occur very rapidly with some compounds. Cheng et al.[108] showed that in certain EDTA complexes a second form of nitrogen was produced in the span of about 1 hr, due to irradiation by X-rays. This resulted in conversion of about half of the surface H_4EDTA nitrogen to a second, possibly, unprotonated form. Zatko and Prather[109] found much faster decomposition of Ag(III) in $Na_5\ H_2Ag(IO_6)_2 \cdot 16H_2O$ by $Mg(K\alpha_{1\,2})$ X-rays. One half of the surface Ag(III) being converted to Ag(I) in about 20 min.

In summary, it can be said that the XPS techniquer with careful attention to the various factors influencing the intensity of the spectral lines, can be of great aid for analysis of bulk

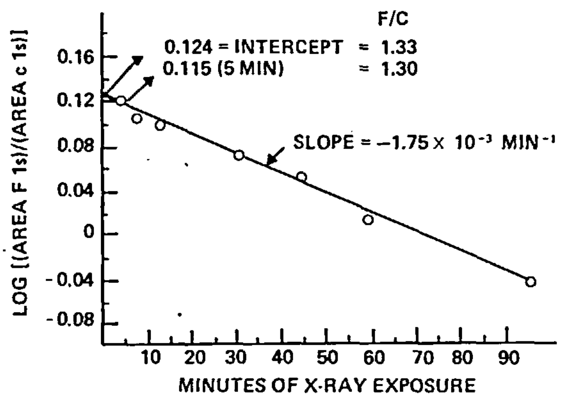


FIGURE 15. Decrease in the F/C ratio for "10-2" MA as a function of X-ray exposure time. (From Phillips, R. W., *J. Colloid Interface Sci.*, 47, 693 (1974). With permission.)

samples. In a few cases (i.e., oxide pairs and polymers) it may be the technique of choice for quantitative elemental or molecular analyses.

C. Trace Analysis

The amount of material studied in an XPS experiment is by the nature of the technique quite small. As discussed in earlier sections, the technique is limited to the very surface of the specimen, sampling only the first 50 to 100 Å at best. Thus, the method is inherently sensitive to very small amounts of any element except hydrogen. Partial monolayers are detectable, as in the case of adsorbed gases. As was shown above, XPS is sensitive to approximately 0.1% for bulk analysis and then only under certain conditions. This sensitivity, however, is such that XPS, at present, is not attractive for use in applications requiring measurement of parts per billion quantities of elements in bulk samples. If experimental methods can be worked out that concentrate the species of interest on the surface of the sample, then the technique will be intrinsically sensitive to 10^{-8} to 10^{-9}g of sample. The papers reviewed in this section deal mainly with concentration of the species of interest with subsequent quantitative analysis in mind.

At first two methods of sample concentration come to mind, the first being some type of electrodeposition of the species of interest onto a metal substrate. Two works involving this technique are known as demonstrated by Brinen and McClure[110] and Zatko et al.[111] Secondly, some type of ion exchange concentration of the sample is made before the XPS experiment. Hercules et al.[112] have experimented with this technique and have developed a unique method for sample concentration.

Much work has been done on qualitative investigation of electrode surfaces, as was discussed in the surface analysis section; however, very little quantitative trace analysis by XPS has been attempted. Brinen and McClure[110] tried multicomponent trace analysis of submicrogram amounts of bismuth, lead, and cadmium. In an attempt to obtain uniform plating on the electrode surface, first a thin film of mercury was plated onto a platinum electrode. Then the metals of interest were plated into this mercury film from a solution of their nitrate salts. The concentrations that were plated onto the electrode were determined by both XPS and anodic stripping voltammetry. The electrodes were either air dried or dried using a heat gun; then the XPS experiment was run. In the case of the air-dried samples both metal and metal oxide were present, with metal oxide being the predominant species. The heat-gun dried samples gave peaks for only the oxides. The amounts deposited in the experiment were 9$\mu g/cm^2$ Bi, 17 $\mu g/cm^2$ Pb, and 3 $\mu g/cm^2$ Cd (Figure 16); these amounts were easily detectable.

The relative intensity of the Cd, Pb, and Bi did not agree with intensity values reported by Wagner.[87] The authors[110] explain this by assuming that some sort of layering occurs during or after deposition or the possibility of Pb and Bi precipitating out of the amalgam. In any event, the Cd lines were very strong, and at least an order of magnitude less cadmium could be detected than was used in these experiments. They show the feasibility of performing multi-component trace analysis of solutions in a single measurement.

Zatko et al.[111] also used the plating technique in an attempt to determine silver electroplated on platinum electrodes. In this preliminary work many problems were encountered, including factors influencing the way the silver was physically plated onto the electrodes. The silver may be plated onto the surface in an irregular fashion, i.e., islands on the surface, long dendrites that protrude from the electrode or on the edges of the electrode (not sampled by XPS). Among the several procedures used to eliminate the above problems were plating from a cyanide bath, using another metal (cadmium) as an internal standard, several different types of pretreatment of the electrodes, and platinizing the electrodes before plating. None of these procedures was successful in producing a plating process that could give reproducible results.

Observing the plating process at constant current, 5 μA for varying times, it was apparent that a great deal of the activity was taking place on the edges of the working electrode, a rectangular piece of platinum foil. In an effort to eliminate this "edge effect" the edges were coated with a

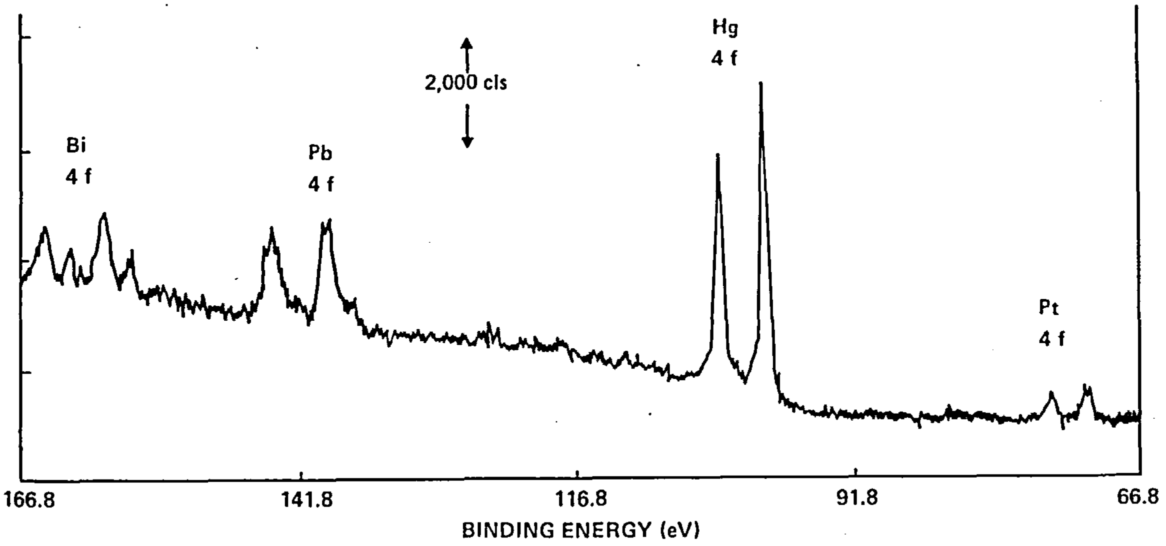


FIGURE 16. ESCA spectrum obtained from an air-dried mercury-coated platinum electrode upon which Bi, Pb, and Cd have been deposited. The strong Cd 3d lines are in a different binding region. (From Brinen, J. S. and McClure, J. S., *Anal. Lett.*, 5, 739 (1972). With permission.)

fast drying epoxy resin. To eliminate variations in electrode surface between different electrodes only one electrode was used. This caused the time of the experiment to greatly increase. Results were then reproducible, as seen in Table 8 and Figure 17. A linear relationship exists between the Ag $3d_{5/2}$ peak heights and the time required for silver deposition. Thus, it is possible to detect submicrogram quantities of silver plated on a platinum electrode in a way that allows for quantitation of the results.

TABLE 8

XPS Ag $3d_{5/2}$ Peak Height Versus Time of Plating

Ag$3d_{5/2}$ Peak Heights (mv X 10^{-2})*	Time of electrolysis (sec) at 5 μA
462	60
748	90
982	120
1600	180

*These values represent the height of the peak in centimeters multiplied times recorder variable Y setting necessary to make the peaks come on scale. These values are averages of at least three runs and are corrected for residual silver.

(From Zatko, D. A., Prather, J. W., and Carney, J. H., unpublished results.)

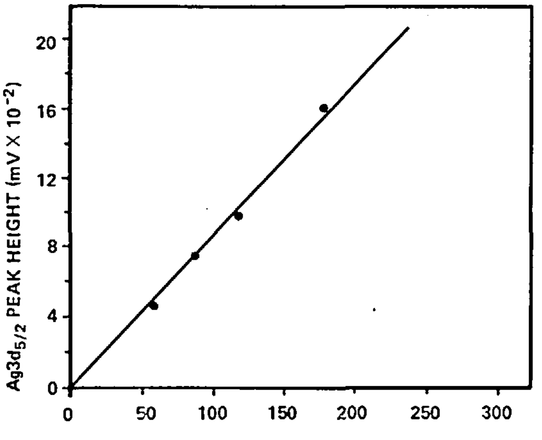
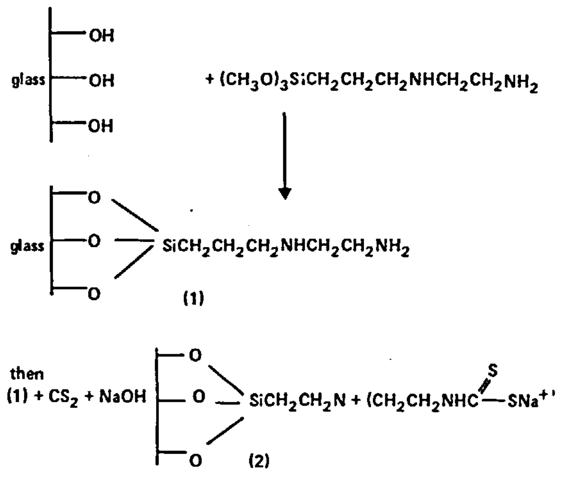


FIGURE 17. Silver $3d_{5/2}$ peak height vs plating time at 5 μA. (From Zatko, D. A., Prather, J. W., and Carney, J. H., unpublished results.)

In the experiments by Hercules et al.,[112] as stated above, a unique method of sample concentration was employed. On first thought, use of TLC or ion exchange resin methods might seem applicable to the problem; but keeping in mind the surface sensitivity of XPS, it is not surprising that these methods fail. What is needed is concentration of the sample only on the surface so as to form a "two-dimensional" array of the species of interest. TLC and ion exchange resins are "three-dimensional" in their surface structure and allow the species of interest to penetrate into their surface thus escaping from detection by XPS. Hercules et al. devised a method to keep the species on the surface by coating glass with a chelating agent thus forming a "two-dimensional" ion exchanger. This type of surface is produced by treating glass fibers in the following manner:



The dithiocarbamate functional group in (2) is capable of reacting with heavy metals as a chelating agent.

Detection limits of approximately 10 ppb of lead, calcium, thallium, and mercury were obtainable. With increased electron spectrometer detection efficiency one would expect this technique to be extended into the parts-per-trillion range for heavy metals. One of the limiting factors would be the K_f of the metal chelate complex; however, by careful selection of the chelating agent the authors[112] propose very selective analytical possibilities for certain metal ions. Introduction of another metal as an internal standard will also produce a means of obtaining quantitative results from this method.

D. Gas Analysis

In this section real and possible applications of XPS to analysis of gaseous or aerosol samples will be discussed. At present, only a few practical applications have been made, all of which deal with analysis of aerosols common in smog and air pollution. Novakov et al.[113] and Novakov[114] participated in the Pasadena Smog Experiment in 1969 in which particulates were collected at various times of the day and in sizes varying from >17 to <0.6 μm. From this study the authors were able to achieve a better understanding of the nature and processes taking place on the particulate matter of which smog is composed by determining the major constituent elements in the particulates, determining the dynamics of chemical change on the particulates, and following the surface chemistry of the particulates. By their use of XPS the authors were able to carry out, in a nondestructive way, experiments *in situ* which were not only semiquantitative, but also gave important information about the distribution of oxidation states for N and S in the particulates.

In the experiment it was found that the sulfur oxidation state distribution was a function of time of day (Figure 18), with S content being highest at night and consisting of S^{4+} and S^{6+}. The S^{4+} predominated at night on the smaller particles and was presumed to be adsorbed as SO_2, which was oxidized to $S^{6+}(SO_4{}^{2-})$ and predominated on the larger particles in the day.

Four types of nitrogen were discernible from the XPS spectra and were postulated to be NO_3^-, NH_4^+, and amino and pyridine nitrogen on the basis of the N ls binding energies. The forms of nitrogen which predominated were found to be the organic type, amino-N, and pyridino-N. The nitrogen content as to amount and oxidation state distribution was also found to have daily periodicity, with the nitrate-N showing a decided preference for the larger (2 to 5 μm) particles (Figures 19 and 20).

In similar experiments Hulett et al.[115] used XPS experiments to follow sulfur content by oxidation state in particulates from various sources (i.e., home fireplace and electrical steam plant

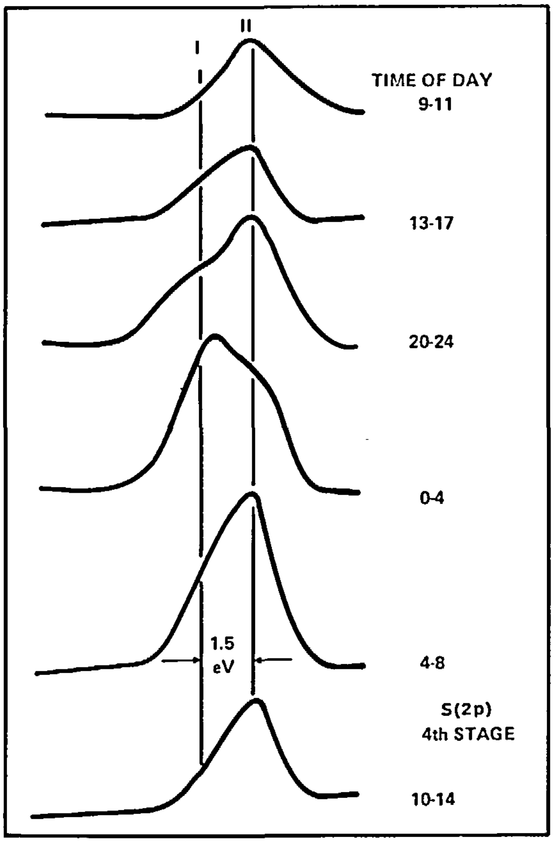


FIGURE 18. Sulfur 2p spectra as a function of the time of day. Component I represents the sulfate and component II represents the sulfite. (From Novakov, T., *Joint Conf. Sensing Environ. Pollutants, Collect. Technol. 1971*, Paper 71-1103, Am. Inst. Aeronaut. Astronaut., New York, 1972. With permission.)

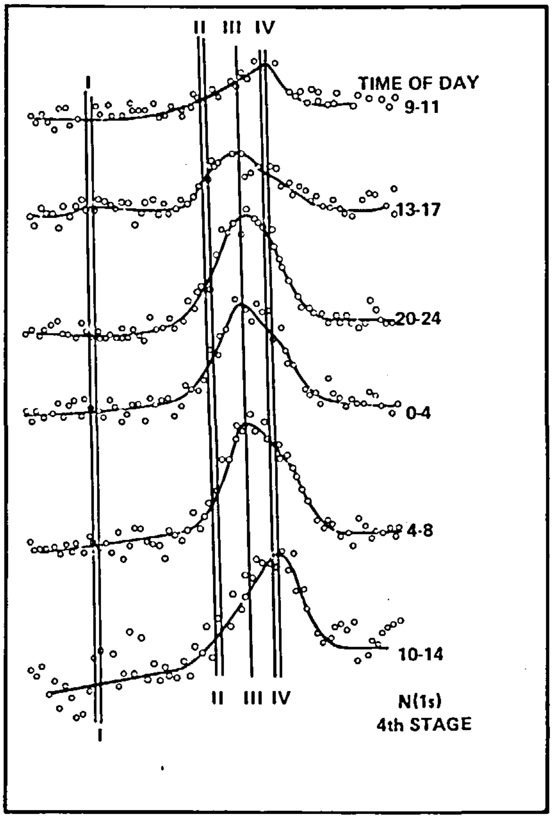


FIGURE 19. Nitrogen ls spectra from the fourth stage samples (MMED = 0.6 μ) as a function of the time of day. Line I is where the nitrate should be found. Intensity scale is arbitrary. (From Novakov, T., *Joint Conf. Sensing Environ. Pollutants, Collect. Technol. 1971*, Paper 71-1103, Am. Inst. Aeronaut. Astronaut., New York, 1972. With permission.)

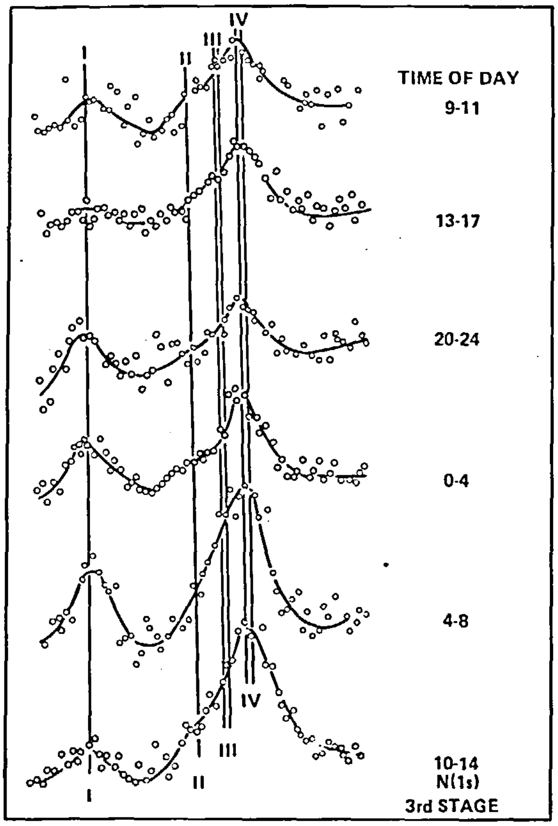


FIGURE 20. Third stage N 1s spectra. Peaks denoted by I, II, III, and IV correspond to nitrate, ammonium, amino- and pyridine-type nitrogens. (From Novakov, T., *Joint Conf. Sensing Environ. Pollutants, Collect. Technol. 1971*, Paper 71-1103, Am. Inst. Aeronaut. Astronaut., New York, 1972. With permission.)

effluents). These authors also found the XPS experiment to be the method of choice for surface analysis of the particulates involved in air pollutants, leading to a more detailed analysis of the interactions between the solid and gaseous phases.

In the experiments involving particulates from the two sources mentioned above it became evident that variation in combustion efficiency could be detected. The sulfur on the particles from the home fireplace was mainly in the more reduced sulfide and sulfite states, while the sulfur from the steam plant effluents was in the more highly oxidized form. This effect arises from the fact that the commercial combustion is more carefully controlled.

Experiments on the interaction of SO_2 with solid surfaces was also carried out. The results showed that the solid involved (i.e., transition metal oxide or alkaline earth oxide) is very important in the oxidation of SO_2 to sulfate. The XPS spectra clearly show the transition metal oxide to be superior for the oxidation of sulfur dioxide to sulfate. Studies of this type will aid in the eventual development of more effective sulfur dioxide abatement processes.

In experiments on air quality done by Araktingi et al.[116] at Louisiana State University, XPS proved to simplify the formidable task of dealing with small quantities of sample and the variety of molecular forms in which the studied elements exist. The experiments were done *in situ*, thus obviating tedious separations and wet chemistry.

From the XPS spectra a qualitative elemental analysis was possible and the following elements were found: O, Al, Fe, Si, S, Pb, Cl, C, Ca, and N. The most pertinent, from the air pollution point of view, were the spectra that indicated the presence of N, Pb, and S. As in the previous examples, varying forms of N and S were encountered, but the most interesting result dealt with lead analysis (Figure 21). The doublets at 139 and

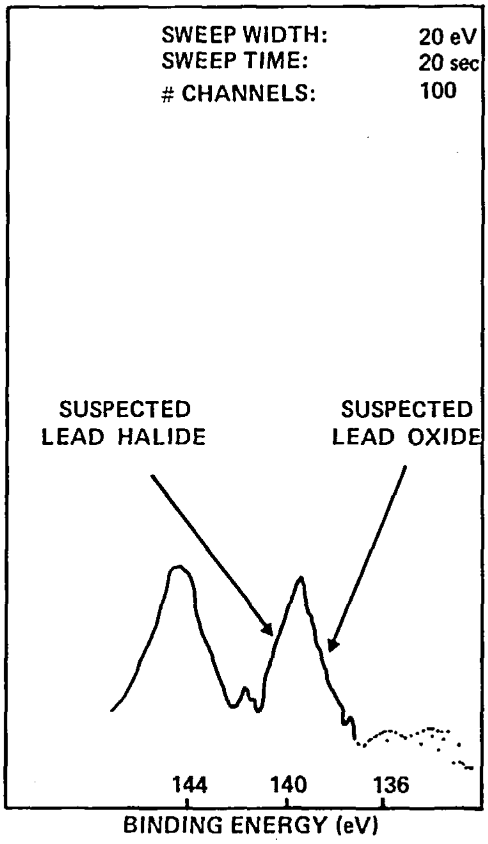


FIGURE 21. Lead 4f spectrum of the particulate sample only. (From Araktingi, Y. E., Bhacca, N. S., Proctor, W. G., and Robinson, J. W., *Spectrosc. Lett.*, 4, 365 (1971). With permission.)

144 eV are due to Pb $4f_{5/2}$ and $4f_{7/2}$ electron emissions, respectively. These lines showed a definite broadening which lead to the hypothesis that Pb was present in more than one form. By careful experimentation (Figure 22), which entailed addition of either pure $PbCl_2$ or pure PbO_2 to the sample, it was determined that two forms of lead were present in about equal amounts, as was proposed earlier from studies of auto exhausts.[117,119] A quantitative analysis was not undertaken. It appears, however, that XPS could be used in a quantitative analysis by more elaborate experiments such as those by Swartz[103] and Kim.[43]

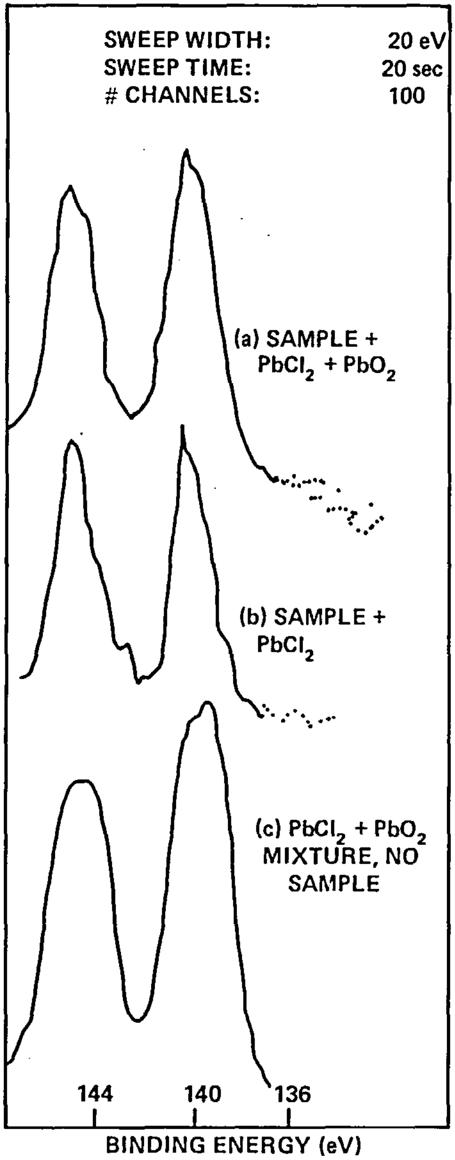


FIGURE 22. Lead spectra of the particulate sample and various lead compounds. (From Araktingi, Y. E., Bhacca, N. S., Proctor, W. G., and Robinson, J. W., *Spectrosc. Lett.*, 4, 365 (1971). With permission.)

There seems to be a growing use of XPS in air pollution research, and this has been reviewed by Hercules.[120] Aside from the above applications, research of a more fundamental nature has been carried on by Siegbahn et al.[8] on the analysis of gas mixtures by XPS. The XPS spectrum shown in Figure 23 demonstrates the ability of XPS to qualitatively distinguish the various components of air. Argon is present at a partial pressure of 1 ppm of atmospheric pressure; however, it is still quite easy to detect. More interesting is the ability of the technique to distinguish between various oxidation states and molecular forms of a given element. In the same manner encountered in the solid state, different oxidation states give rise to shifts in the XPS lines, thus offering a tool for distinguishing various components in a mixture even though the compounds involved are quite similar (Figures 24 and 25).

Even though the XPS technique is not as sensitive as mass spectroscopy, it gives data that are complementary to those obtained from mass spectroscopy. One can envision a large area of work where elemental and oxidation state analysis of gases would be very useful indeed, not to mention the data on atomic and molecular orbital energies obtained from the XPS experiment. Work on gases with X-ray excitation is a field in which comparatively very little work has been done. Apparently, there are some problems with sensitivity and variations in intensity of the peaks with pressure; however, quantitative gas analysis may be possible in the future.

E. Special Applications

In this section novel uses of photoelectron spectroscopy will be discussed in an attempt to show unusual uses of the technique to aid in analyses. The most unusual application of photoelectron spectroscopy to date must be the experiments by Mukai and Hirao[121] in which a photoelectron spectrometer aboard the sounding rocket K-9M-40 was launched from Uchinouwa, Japan on September 20, 1972 at 1,400 hr JST. During the experiment photoelectrons produced through the ionization of the upper atmospheric constituents by the solar ETV radiation were measured, during

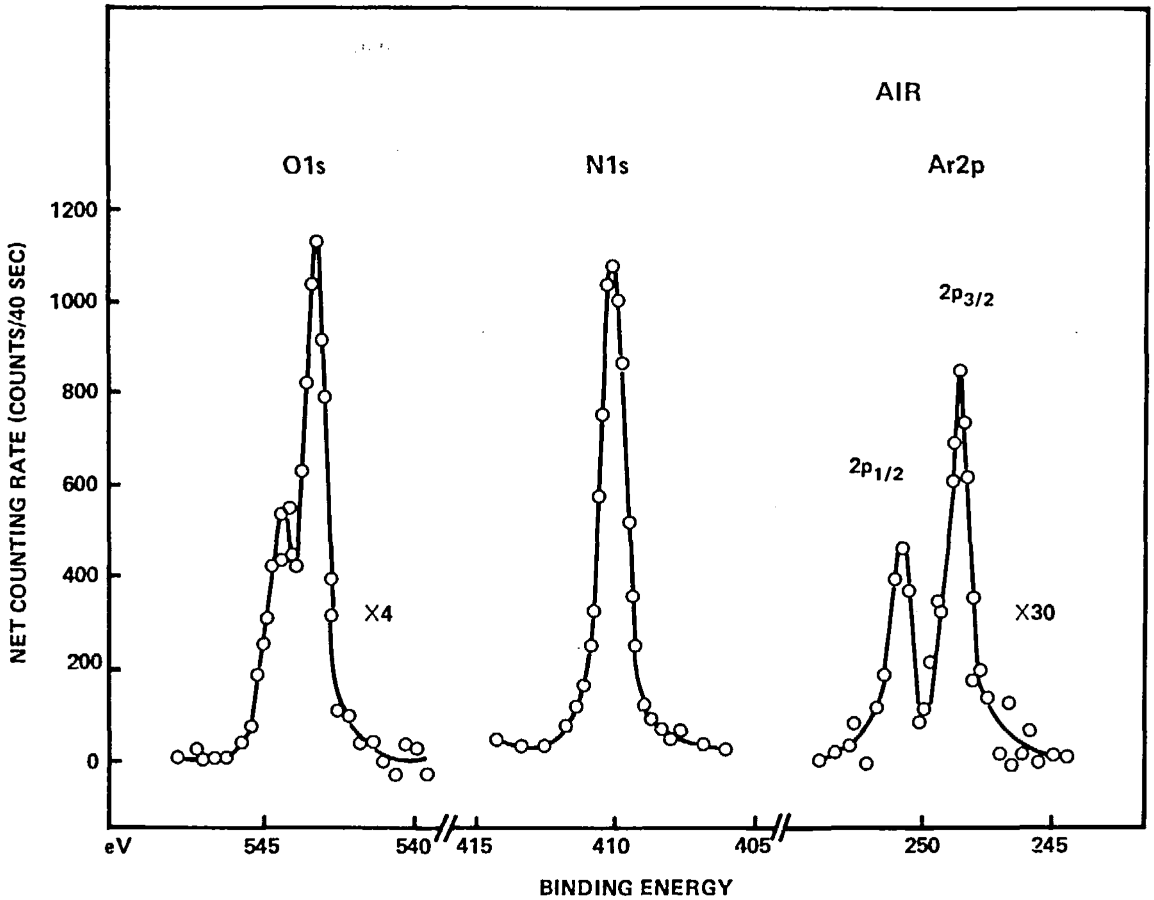


FIGURE 23. ESCA spectrum from air excited by Mg Kα radiation. The oxygen 1s line shows spin splitting (paramagnetic molecule). Argon is detected through its 2p electrons and the spin-orbit splitting is well-resolved. (From Turner, D. W., Baker, C., Baker, A. D., and Brundle, C. R., *Molecular Photoelectron Spectroscopy*, John Wiley & Sons, New York, 1970, 10. With permission.)

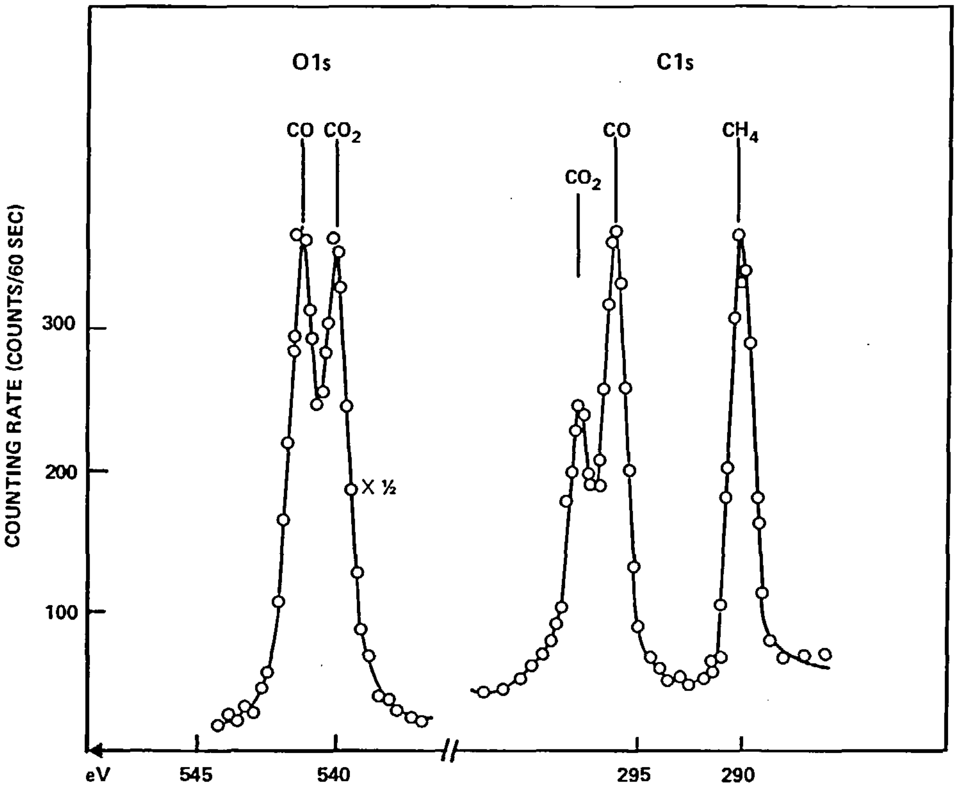


FIGURE 24. ESCA spectrum from a mixture of the gases CO, CO_2, and CH_4. (From Turner, D. W., Baker, C., Baker, A. D., and Brundle, C. R., *Molecular Photoelectron Spectroscopy*, John Wiley & Sons, New York, 1970, 13. With permission.)

the ascent, between 160 to 315 km. Knowledge about the kinetic energy distribution of photoelectrons in the ionosphere was obtained.

As one might imagine, many technical problems were encountered, but the spectra obtained (as shown in Figure 26) compared well with at least one set of theoretical calculations (Figure 27). The point of interest was the observation of fine structure not observed by other experimental techniques or predicted by the majority of the calculations. From these results a better idea as to the photoelectron yield from atomic oxygen and molecular nitrogen bombarded by solar He(II)304 Å radiation was obtained. With refinement of the technique new studies of the earth's atmosphere may reveal results of a more analytical nature. This would lead to a better understanding of processes in the atmosphere and perhaps lead to some monitoring system for upper atmospheric pollution.

In the next application a tough technical problem has been dealt with in a very satisfactory way. The problem has been how to run XPS experiments on liquids. In the past this was only possible by freezing the liquids or solutions or doing experiments on the gas phase of such liquids. Now, Siegbahn and Siegbahn[122] present a technique that facilitates XPS spectra of liquids and solutions in the liquid phase, thus eliminating problems involved in working with frozen solutions. Figure 28 shows the experimental setup used to produce the liquid beam that makes the technique work.

As one might imagine, the experimental procedure has many variables and conditions to be dealt with. Siegbahn and Siegbahn[122] list them as follows:

1. The liquid beam must be produced under conditions of nonturbulent flow with no droplets.
2. The beam should be small in diameter and pass close to the entrance slit of the spectrometer.

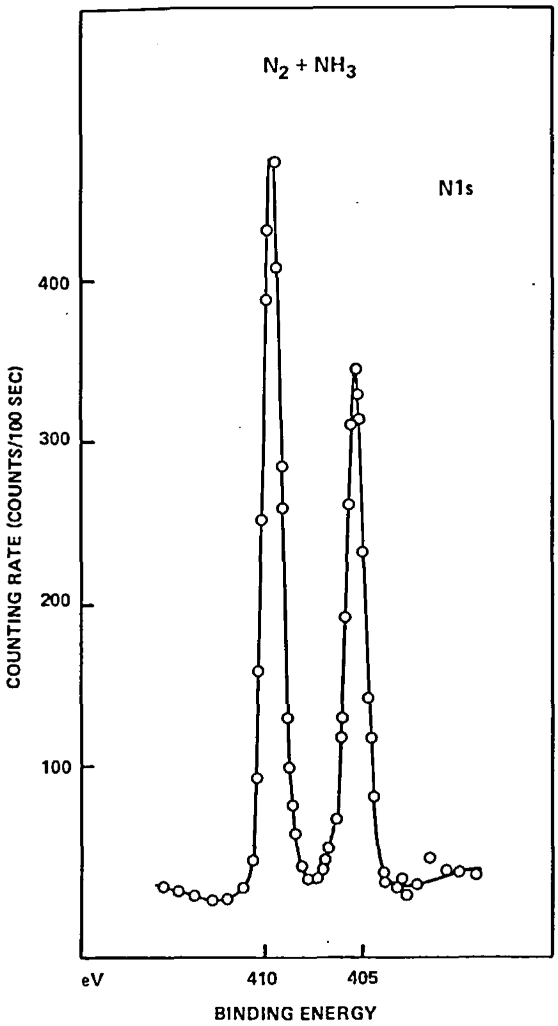


FIGURE 25. Nitrogen 1s lines from a mixture of nitrogen gas and ammonia. The ammonia line is shifted towards lower binding energy due to the charge transfer from the hydrogen atoms. (From Turner, D. W., Baker, C., Baker, A. D., and Brundle, C. R., *Molecular Photoelectron Spectroscopy*, John Wiley & Sons, New York, 1970, 12. With permission.)

3. Any droplets formed must be prevented from depositing on the X-ray window or entrance slit.

4. Efficient differential pumping must be maintained.

5. Part of the beam facing the entrance slit must be exposed to X-rays.

6. It should be possible to distinguish between those electrons that originate from the vapor and liquid phase.

7. In order to reduce the liquid's vapor pressure, it must be precooled.

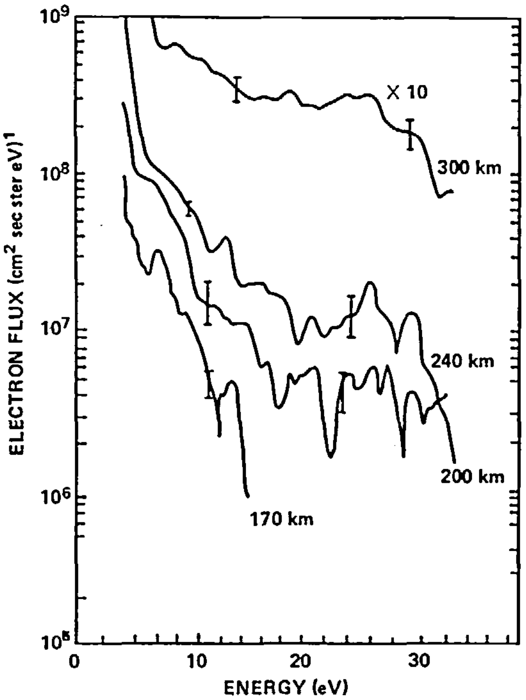


FIGURE 26. Energy spectra of the photoelectron flux. Each spectrum represents an average over the vertical distance of ~30 km. Error bars represent ± 1 standard deviation in the electron flux. (From Mukai, T. and Hirao, K., *J. Geophys. Res.*, 78, 8395 (1973). Copyright by American Geophysical Union. With permission.)

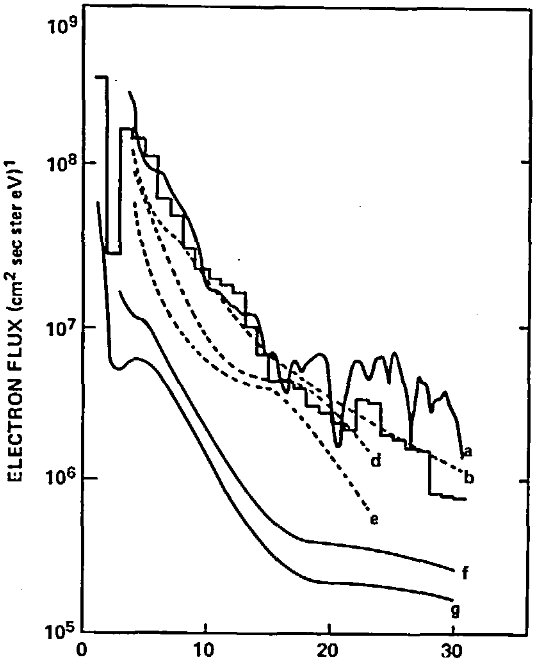


FIGURE 27. Comparison of this work with other observational and theoretical spectra at the ~200-km level. (From Mukai, T. and Hirao, K., *J. Geophys. Res.*, 78, 8395 (1973). Copyright by American Geophysical Union. With permission.)

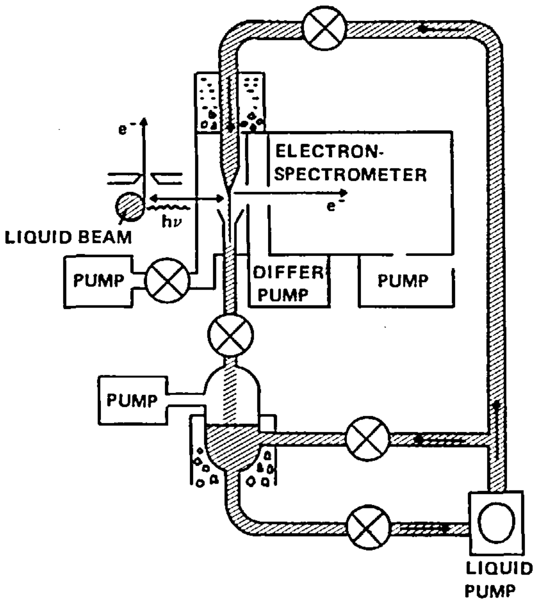


FIGURE 28. Principle of the liquid beam arrangement. (From Siegbahn, H. and Siegbahn, K., *J. Electron Spectrosc. Relat. Phenom.*, 2, 320 (1973). With permission.)

8. To reduce the amount of liquid required for long run times, recirculation is necessary.
9. One has to be cautious about any possible charging of the liquid beam due to friction at the nozzle.

Even with all these conditions, XPS spectra can be taken. Many organic solvents have sufficiently low vapor pressure (1 torr), in particular, formamide, triethyl phosphate, dimethylacetamide, and hexamethylphosphorotriamide. Also, the possibility of heating solids above their melting point must be considered.

As can be seen in Figure 29, alignment of the liquid beam is critical to exclusion of photoelectrons arising from the vapor phase. Thus, the beam position must be adjustable during the actual experiment.

Figure 30 shows spectra of 2 *M* KI dissolved in formamide. The iodine and potassium give strong lines in 20 min.

The same conclusions can be drawn here as the case of frozen solutions (i.e., many unisolatable solutes can now be investigated and, perhaps by mixing two solutions just before entering the sample chamber, reaction intermediates may be studied).

The final application discussed here makes an ingenious manipulation of the basic photoelectron equation:

$$E(\text{kinetic E of photoelectron}) = h\nu - E(nl) \qquad (2)$$

Thus, if the kinetic energy of a photoelectron arising from an energy level (n, l) of some target atom is known, then the wavelength of the ionizing energy may be calculated. By use of the above method a photoelectron spectrometer may be used as a detector system in X-ray analyses. The method was named PAX, photoelectron spectrometry for analysis of X-rays, by Krause,[123] who presented the first work in this area. With PAX a novel energy-dispersive technique is introduced, combining several advantages of the conventional techniques (specifically, the high resolution of wavelength-dispersive grating and crystal spectrometers and the well-defined intensity characteristics of nondispersive or energy-differentiating proportional counters, solid state detectors, and scintillators).

The PAX technique as described by Krause makes use of a target gas, usually He or Ne, that has naturally occurring well-defined energy levels. The target gas is bombarded with X-rays emitted from an X-ray tube which has for its anode the sample material. The energy of the photoelectrons produced in this manner is then compared with that of photoelectrons produced by standard X-rays from anode materials of the following atoms: Y, Zr, Nb, and Mo. Photoelectron lines from the standard atoms, along with their FWHM, are shown in Figure 31.

If one measures the difference in kinetic energy, ΔE, for two different X-ray anode materials, then

$$\Delta E = [h\nu - E(nl)] - [h\nu_0 - E(n'l')] \qquad (3)$$

and the x-ray energy is then obtained from

$$h\nu = \Delta E + h\nu_0 \qquad (4)$$

$$E(nl) = E(n'l') \qquad (5)$$

$$h\nu = \Delta E + h\nu_0 - [(E(n'l') - E(nl)] \qquad (6)$$

$$E(nl) \neq E(n'l'). \qquad (7)$$

The number of photons was also related to the

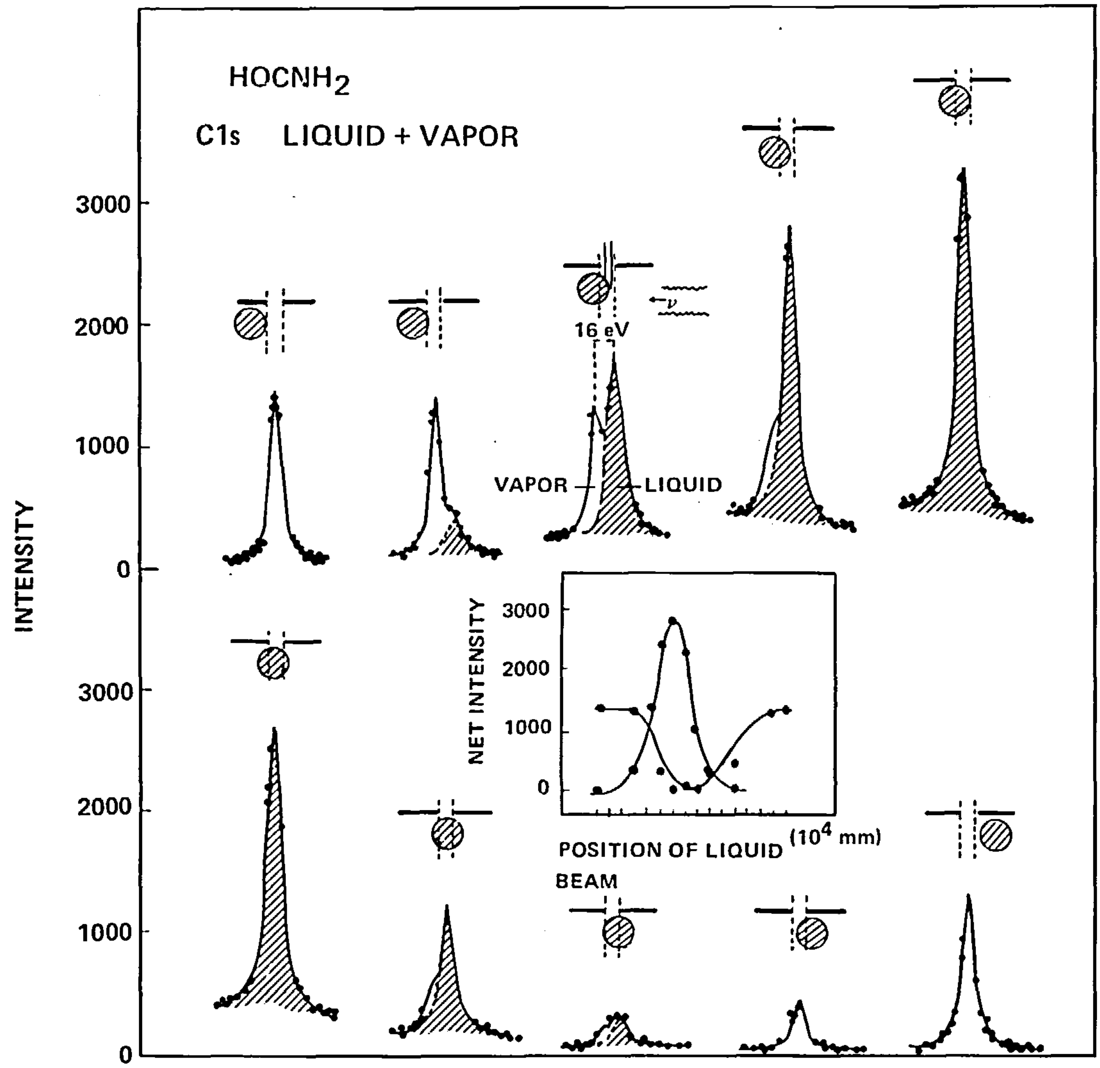


FIGURE 29. ESCA lines from the C 1s level in formamide ($HOCNH_2$) as a function of liquid beam position. There is a splitting of the line of 1.6 eV because of a difference in C 1s binding energy for the liquid and the vapor. At a certain position of the liquid beam the signal from the vapor is completely suppressed. (From Siegbahn, H. and Siegbahn, K., *J. Electron Spectrosc. Relat. Phenom.*, 2, 322 (1973). With permission.)

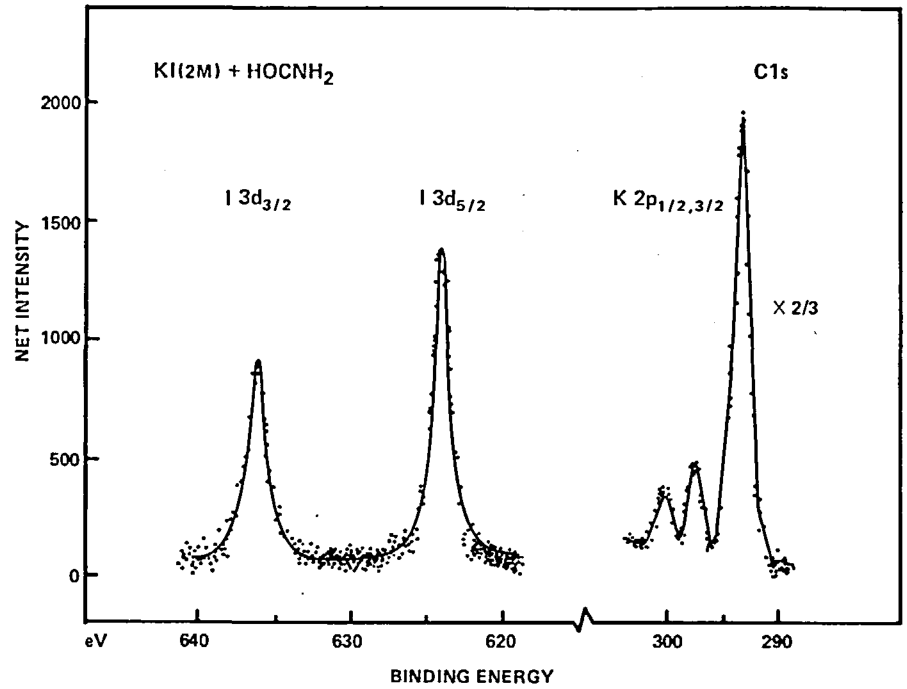


FIGURE 30. ESCA lines due to iodine and potassium in KI dissolved in formamide from the 3d$_{3/2}$ and 3d$_{5/2}$ levels of I and 2p$_{1/2}$ and 2p$_{3/2}$ levels of K. The C 1s line from the liquid HOCNH$_2$ happens to come close to the K 2p$_{1/2,3/2}$ doublet. (From Siegbahn, H. and Siegbahn, K., *J. Electron Spectrosc. Relat. Phenom.*, 2, 324 (1973). With permission.)

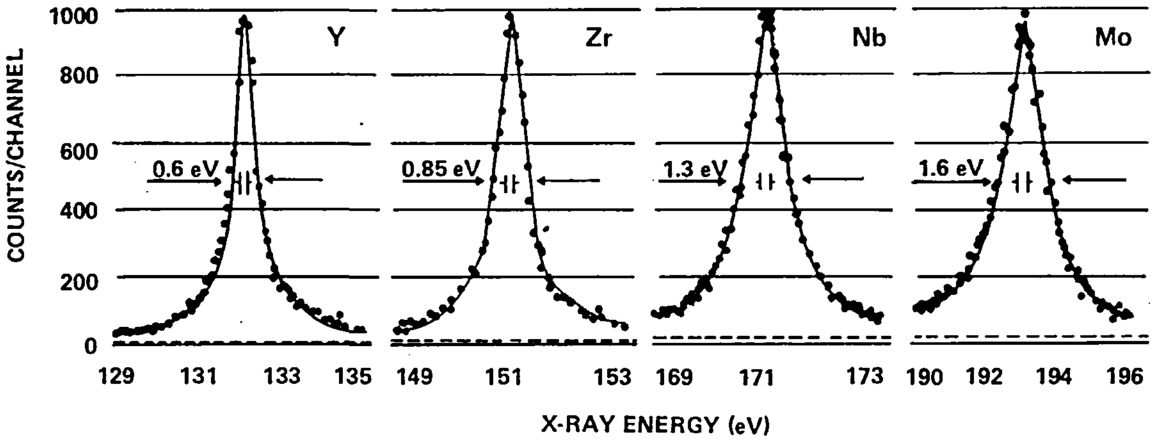


FIGURE 31. Mg lines of yttrium to molybdenum. 4 KV-20 mA electron excitation; recording time about 10 min/line. (From Krause, M. O., *Adv. X-Ray Anal.*, 16, 84 (1973). With permission.)

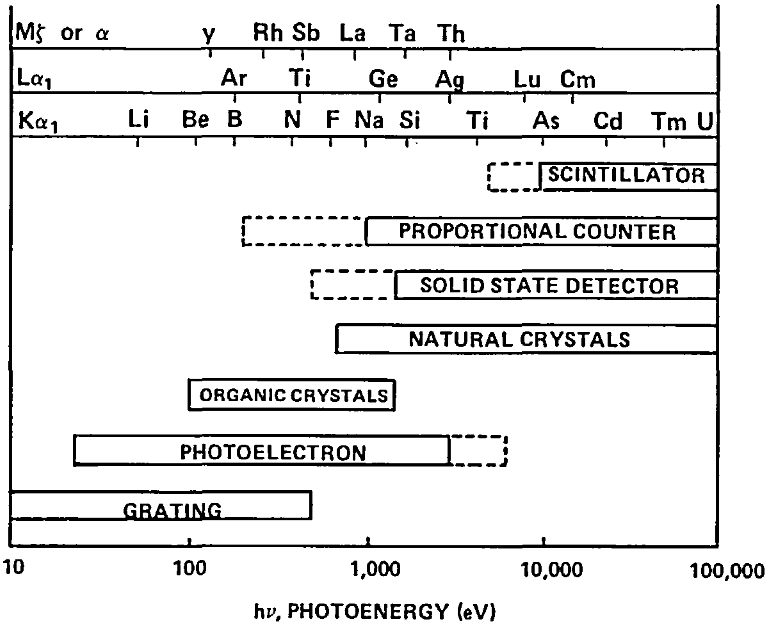


FIGURE 32. Typical ranges of various X-ray spectrometers. Dash bars indicate special purpose ranges. (From Krause, M. O., *Adv. X-Ray Anal.*, 16, 81 (1973). With permission.)

number of photoelectrons; equations were given through which absolute intensity of the X-rays may be determined, thus making PAX a quantitative as well as qualitative tool.

The useful energy range of PAX is quite broad, extending from about 20 eV to almost 10 KeV. Its range is compared with those of other techniques as shown in Figure 32.

F. Calibration of XPS Spectra

Chemical shifts have analytical significance in XPS in as much as the nature (i.e., oxidation state) of the chemical species can be accurately determined through measurement of changes in the binding energies of inner core electrons. Changes in the valence shell electron density are reflected in the inner core levels. This effect is attributed to the fact that as valence electron density changes so does the effective atomic charge, which in turn causes fluctuation in all electron energies within the atom. Measured values of the kinetic energy of photoejected electrons then reflect these changes in the core levels.

As one might imagine, electrons leaving through the photoemission process leave behind a positive charge. This represents no problem if the sample is a conductor that is well-grounded; however, in the case of a nonconducting sample, how is this charge to be dissipated? In the simplest case that might be set forward, the result of an ever-increasing positive charge would be to make the escape of electrons from the surface more difficult with time of irradiation, thus causing the kinetic energy of ejected electrons to decrease with increasing time of X-ray exposure. Fortunately, this is not what actually occurs. Since the sample is in close proximity to the X-ray tube window, which is a source of low energy electrons, a steady state is reached in which the sample is partially discharged. This is in itself a problem since the degree to which the positive sample charge is dissipated is dependent on the rate of electronic photoemission, which is in turn dependent on the characteristics of the sample material. Different elements have different photoejection cross-sections and, thus, different rates of photoemission. Corrections for this charging effect have been the basis for much research and will be covered in this section.

Attempts to correct for the charging effect generally fall into two categories, the first being methods of reducing the sample charge and the second being efforts to correct for the charge by use of internal standards.

For the first area the most notable work was done by Huchital and McKeon[124] in an experiment in which the authors added an electron "flood gun" to their spectrometer. The "flood gun" consisted of a tungsten filament arranged as to bombard the sample with low energy electrons. They found a definite dependence of peak position and peak width with "flood gun" current, shown in Figures 33 and 34. This dependence was observed for both gold islands on glass and Teflon® samples. In the use of such an arrangement, however, one must be cautious, as it is possible to create a negatively charged sample which would also hinder the determination of accurate absolute kinetic energies.

A report of work by Dickinson et al.[125] also deals with methods for charge correction that essentially aim at reducing the sample charge. In this work on "intermediate" conductors, such as silver iodide (2×10^{-5} ohm $^{-1}$ cm^{-1} ionic conductivity), variation in sample mountings, the size and polarity of a bias potential, and X-ray beam flux were seen to cause changes in both peak position and peak width. A very important observation was made concerning the use of metal grids as sample mounts. The use of such grids is an effort to bring the majority of sample in contact with ground thus reducing the charge. The authors found, however, that the peak width would increase if a negative bias was applied to the grid. This was explained in terms of differential sample charging. That is, in each grid square the sample will experience a potential gradient, thus causing a broadening in the range of kinetic energies of electrons emitted from the sample. With very high bias potentials the Ag $3d_{5/2}$ peak breadth was greater than two Ag $3d_{5/2}$ lines.

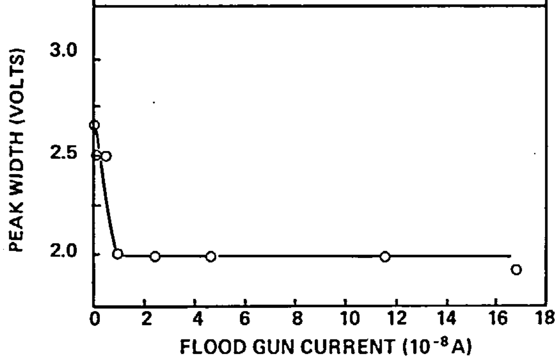


FIGURE 33. Dependence of peak position and peak width on flood-gun current for a sample consisting of gold islands on glass. (From Huchital, D. A. and McKeon, R. T., *Appl. Phys. Lett.*, 20, 159 (1972). With permission.)

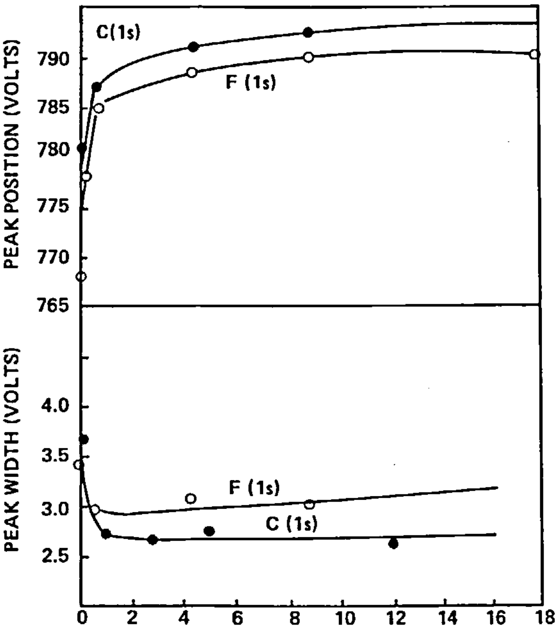


FIGURE 34. Dependence of peak position and peak width on flood-gun current for a Teflon® sample. (From Huchital, D. A. and McKeon, R. T., *Appl. Phys. Lett.*, 20, 159 (1972). With permission.)

In the same set of experiments a small puncture was made in the X-ray source window. With the hole present none of the charging effects studied were observed, thus pointing again to the possible use of electron "flood gun" control of sample charging.

Another method for reducing the charge on the sample was presented by Counts et al.[126] in their work on lead absorbed on montmorillonite. In this report the authors pressed their sample into indium foil, and found this to be a satisfactory way of reducing charge; however, no detailed study of how well this procedure worked was given.

If the sample charge cannot be reduced to a negligible value, then some other method for compensation must be found. In this area research has been focused on a suitable internal standard to either be mixed with or deposited on the surface of the sample. This standard material should do two things: be inert to reaction with the sample and closely follow the charge fluctuations of the sample. One must also know the absolute value for the binding energy of the standard line. In order to make such an absolute measurement the energy scale for the spectrometer must be known. One way to do this would be to irradiate a conducting sample, such as gold, with two wavelengths of X-rays (Al Kα and Mg Kα); two gold spectrums will arise, differing in energy by the energy difference of two source radiations. The energy of the X-rays are accurately known and thus an energy scale can be established. Once the scale is known the absolute position on this scale can be obtained by either referencing the line to the Fermi level (taken as zero KE) or to some well-characterized Auger line. Several papers discussing methods of calibrating the spectrometer have been given.[7,127,128] One paper that goes into some detail has been presented by Johansson et al.[129]

Many compounds have been used as internal standards. This creates a problem when comparing works done in reference to different standards. The first standard proposed by Siegbahn[7] was the carbon 1s line arising from "pump oil" deposited on the sample surface during the experiment. This line from carbon contamination is always present and seemed well suited for use as a standard; however, there have been several objections to this C 1s line as a standard. First, the nature of the carbon contaminant is unknown. Thus, one cannot really be sure what the reference is. In addition, the contaminant can vary from laboratory to laboratory. Finally, there is no clear-cut evidence that the contaminant actually follows the sample's charge fluctuations. In its favor, however, is the fact that it works generally well, is inert to most samples, and is already in wide usage. Nordberg et al.[130] have suggested mixing graphite with the sample and using that C 1s line as standard. Stec et al.[131] have used Pb_3O_4 as an internally mixed standard, and their results for arsenic binding energies agree well with those found by Hulett and Carlson[132] who used KCl as their reference. Jack and Hercules[133] and Swartz and Hercules[134] found that the best results were obtained by using a standard chemically similar to the compounds being studied (i.e., the N 1s from KNO_3 was used as the standard in a study of quartenary nitrogen and P 2p line from $Na_4P_2O_7$ was used in a study of phosphonium compounds). Along this same line Ogilive and Wolberg[135] have had success in using the Al 2p line for work on metal oxide catalysts supported on alumina.

An alternate method to mixing the reference with the sample is to deposit a thin noncontinuous layer of noble metal on the sample surface.[136-138] There have been several comparisons made between deposited gold and other mixed references. Swartz et al.[139] found MoO_3 to be superior to gold for use in six-coordinate tin compounds, the proof being that the values for Sn $3d_{5/2}$ binding energy referenced to MO $3d_{5/2}$ peak gave a better correlation to the Mössbauer isomer shifts than did values obtained with the gold reference.

Davis and Lester[140] have compared MoO_3, gold, and contaminant carbon and found MoO_3 to be lacking in that its peaks were not shifted by exactly the amount of a charge (-5 V) applied to the sample. Carbon and gold, on the other hand, did shift by exactly the amount of applied voltage. Thus, the authors suggested that any internally mixed standard will fail to give good results if it is nonconducting. They also failed carbon contaminant as a reference on the same grounds as stated above, namely, that it is from unknown sources.

It would seem that gold, either mixed as a dust or deposited on the sample surface, would be the only standard of any utility that remains; however, gold also has its problems. First, there is no agreement on the exact value of the Au $4f_{7/2}$ line with at least three different values being reported.[7,141,142] Secondly, reports of gold-sample interaction have been given by Betteridge et al.[143] These authors have found the gold 4f spectra to be quite complicated as well as temperature dependent for samples such as KCN, NaCl, $Na_2S_2O_3$, and copper phthalocyanine, as can be seen Figure 35. The intensity and complexity of the gold spectrum was also found to be dependent on deposition time, as shown in Figure 36. The dangers involved in using gold as a reference have also been pointed out by Matienzo and Grim[144] in their work on various phosphorous complexes. They found the gold to be reliable when used to measure complexed phosphines, but when attempts were made to measure the binding energies of the free ligands, gold was found to be unsuitable due to complex formation between free phosphine ligand and deposited gold (Figure 37).

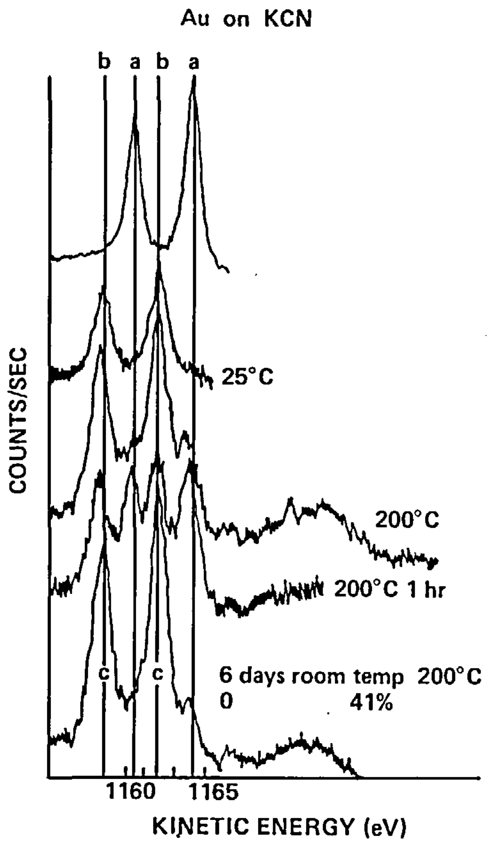


FIGURE 35. Electron spectrum of vacuum-deposited gold on potassium cyanide. From top to bottom: Top = metallic gold at 25°C; Second = gold on KCN at 25°C (a = 0%, b = 100%); third = gold on KCN at 200°C (a = 31%, b = 69%); Fourth = gold on KCN at 200°C for 1 hr (a = 58%, b = 42%); Bottom = gold on KCN at 25°C for 6 days, then heated to 200°C for several hours (a = 16%, b = 41%, c = 43%). Pairs of gold peaks: a = 1160.4, 1164.1 eV; b = 1158.5, 1162.3 eV; c = 1158.3, 1162.0 eV. (From Betteridge, D., Carrer, J. C., and Hercules, D. M., *J. Electron Spectrosc. Relat. Phenom.*, 2, 329 (1973). With permission.)

Ginnard and Riggs[145] have demonstrated that use of gold on polymer surfaces can create errors of 0.6 eV. This is due to the dependence of surface charge on the amount of gold deposited. The gold has a larger cross section for photon absorption than the other elements in the polymer and thus gives rise to a greater photoelectron flux leaving the sample. As one increases the gold coverage, the amount of photoelectrons leaving the surface (and thus the surface charge) increases. Thus, binding energy is a direct function of gold coverage (Figure 38).

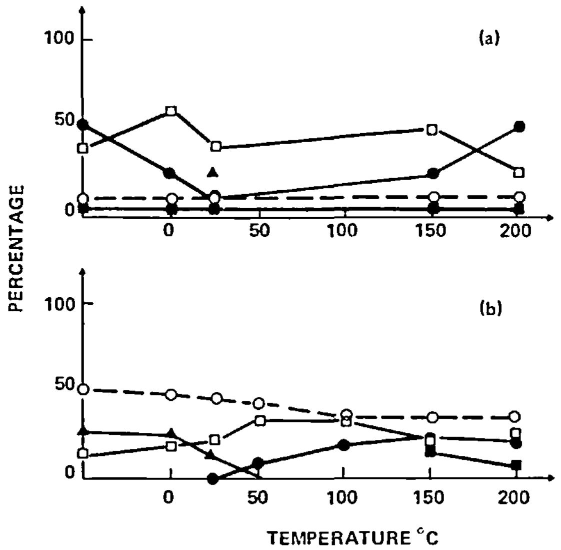


FIGURE 36. Effect of deposition time and temperature on the relative intensities of gold, vapor deposited on copper phthalocyanine. (a) 10-sec deposition of gold; kinetic energies of Au $4f_{7/2}$ (eV) ○, 1160.4; ▲, 1163.3; □, 1164.1; ●, 1165.3; ■, 1167.1. (b) 15-sec deposition of gold; kinetic energies of Au $4f_{7/2}$ (eV) ○, 1160.4 (a in figure 35); ▲ 1161.2 (b in Figure 35); □, 1162.3 (c in Figure 35); ●, 1163.5 (d in Figure 35); ■, 1160.5 (e in Figure 35). (From Betteridge, D., Carrer, J. C., and Hercules, D. M., *J. Electron Spectrosc. Relat. Phenom.*, 2, 332 (1973). With permission.)

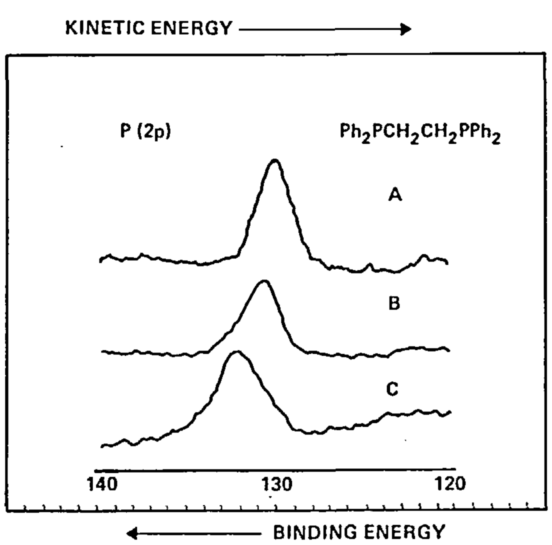


FIGURE 37. P 2p XPS spectra of bis(diphenylphosphino)ethane before and after treatment with gold vapor. (A) Sample without any gold; (B) Sample with gold deposited onto one section of the sample; (C) Sample after deposition of gold by rotation of the sample. No charging corrections have been incorporated. (From Matienzo, L. J. and Grim, S. O., *Anal. Chem.*, 46, 2053 (1974). Copyright by the American Chemical Society. With permission.)

The results of the studies cited above give insight into the problem of standards, but leave the question of which standard is best open-ended with no apparent solution. The only suggestion that has been made is to use several standards for each sample, a common practice in UV photoelectron spectroscopy.[143] An approach similar to that used by Kumar et al.,[146] who used graphite, NaCl, and palladium as references in a study of palladium complexes, may be the best method.

III. ULTRAVIOLET MOLECULAR-PHOTOELECTRON SPECTROSCOPY (UPS)

A. Qualitative and Quantitative Applications

The area of photoelectron spectroscopy using the He(I), (II) discharge lamp as its ionizing radiation has come to be known as UV photoelectron spectroscopy or UPS. The range of energy covered is 0 to 21.21 eV and 0 to 40.8 eV for the

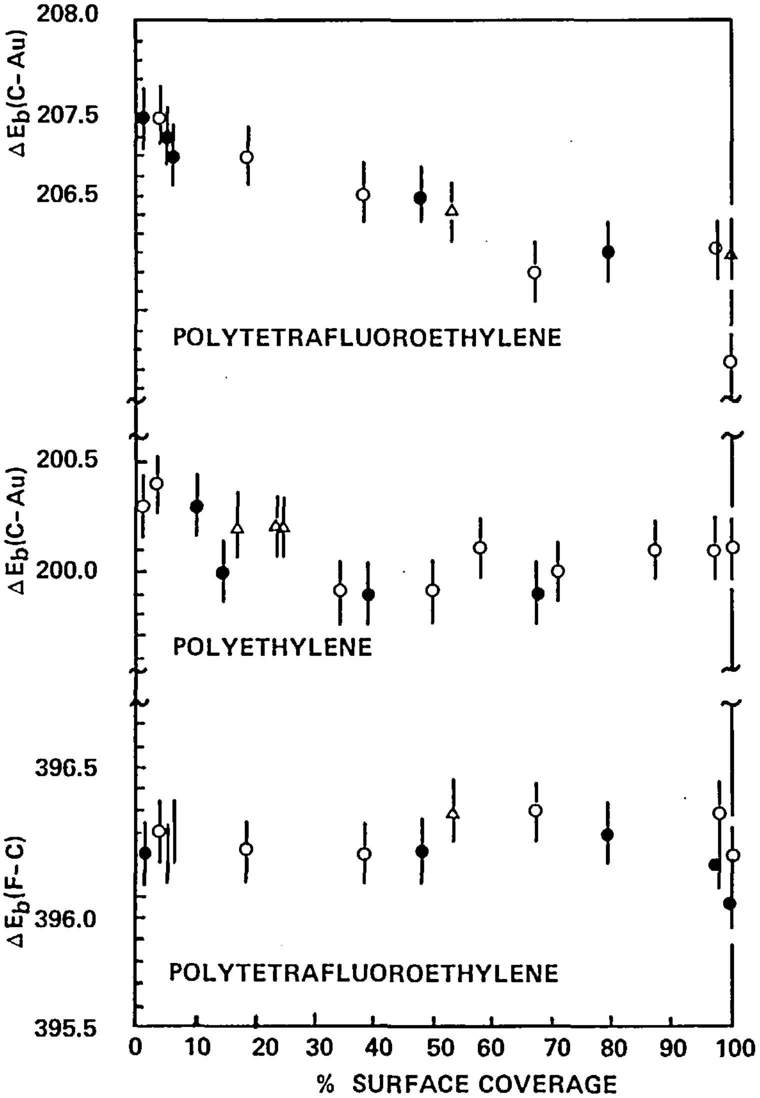


FIGURE 38. Core level binding energy differences for gold on PTFE and PE vs percent surface coverage. (From Ginnard, C. R. and Riggs, W. M., *Anal. Chem.*, 46, 1308 (1974). Copyright by the American Chemical Society. With permission.)

He(I) and He(II) resonance lines, respectively. These resonance lines are produced by either a microwave or electrical discharge in small quartz capillaries. Very pure helium is required to obtain best results as shown by Cairns et al.[147] This requirement being met, only photoelectrons due to one wavelength of radiation are present.

Since the natural line width of the He resonance line is very small when compared to the energy difference between most vibrational states, a detailed picture of the highest occupied molecular orbitals of a compound may be obtained. It is this fact along with the range of energies involved that separates XPS and UPS. UPS, being quite sensitive to change in the outer molecular orbitals, can give results that are of great theoretical importance with respect to calculations of these energies and is the first experimental technique capable of directly giving more than just the first ionization potential. It is, however, sensitive to different elements in a very limited sense; that is, only if the element has "nonbonding" electrons, in which case very sharp lines are observed. In this way, the presence of halogen, S, P, Se, Te, O, and in some instances N can be determined with little difficulty. This, coupled with the fact that the gas phase is at present the best state of the sample to be analyzed, may indicate that UPS will be limited with respect to analytical chemistry. There are, however, mitigating circumstances. The technique is quite sensitive, more than IR or NMR but less than mass spectrometry, and sufficient differences in the spectra of related compounds are present to allow for molecular identification. In some cases even structural isomerism may be detected.[13]

Several review articles have appeared that are of interest to the analytical chemist.[12-14] Few attempts at analytical applications of UPS as compared to those of XPS have appeared in the literature, and these will be reviewed below.

At present there is no law, similar to Beer's Law, that correlates UPS intensities with concentration of a given species. In fact, UPS peak intensities are dependent on many factors, two of the most prevalent being the general nature of the molecular orbital from which the ionization is occurring and the wavelength of the radiation used.[148] That is to say, the cross section for photon-electron interaction is a function of the exciting radiation. This and the nonlinearity of transmission for varying kinetic energy (high kinetic energy being favored) for most instruments[13] makes peak intensity of little use until a better understanding of UPS cross sections is worked out. By use of calibration curves, however, some meaningful data may be obtained. The salient point to be understood is that very little work has been done.

Daintith et al.[149] were able to use the technique to analyze commercial samples of COS. When the carbon oxysulfide was subjected to mass spectral analysis, impurities of 1.5% CS_2 and 4.4% CO_2 were found; however, when UPS spectra were taken, only trace amounts of these compounds were observed. By addition of known proportions of CO_2, CS_2, and COS the authors were able to calibrate their instrument and found $\ngtr$0.2% CS_2 and 0.1% CO_2. They suggest that a disproportionation of COS to CO_2 and CS_2 was occurring on the hot filament in the mass spectral analysis (Figure 39).

A very good discussion of the analytical aspects of UPS has been presented in an article by Betteridge[150] in which he states his *prima facie* case for the importance of UPS as an analytical tool. Criteria for testing UPS acceptance as such a tool were stated as follows:

1. that the spectrum of a compound should be unique;
2. that the spectrum should be capable of fairly easy interpretation;
3. that the information should be different from and/or supplement that obtained from other techniques and/or it should be obtained on a significantly smaller sample;
4. that it should be applicable to a wide range of compounds; and
5. that the technique should be capable of handling samples on a routine basis.

He presents good evidence that criteria 1, 2, 4, and 5 are met. By use of correlation diagrams like Figures 40 and 41 it is easy to see that sufficient uniqueness of spectra is present and that a wide range of compounds is accessible to the technique. As for ease of interpretation, this can be quite difficult if one must assign the origin of each line; however, as in IR, this is not necessary when qualitative analysis is the goal.[151] When more than one compound is present in significant proportions interpretation becomes more difficult; however, anyone familiar with the technique can

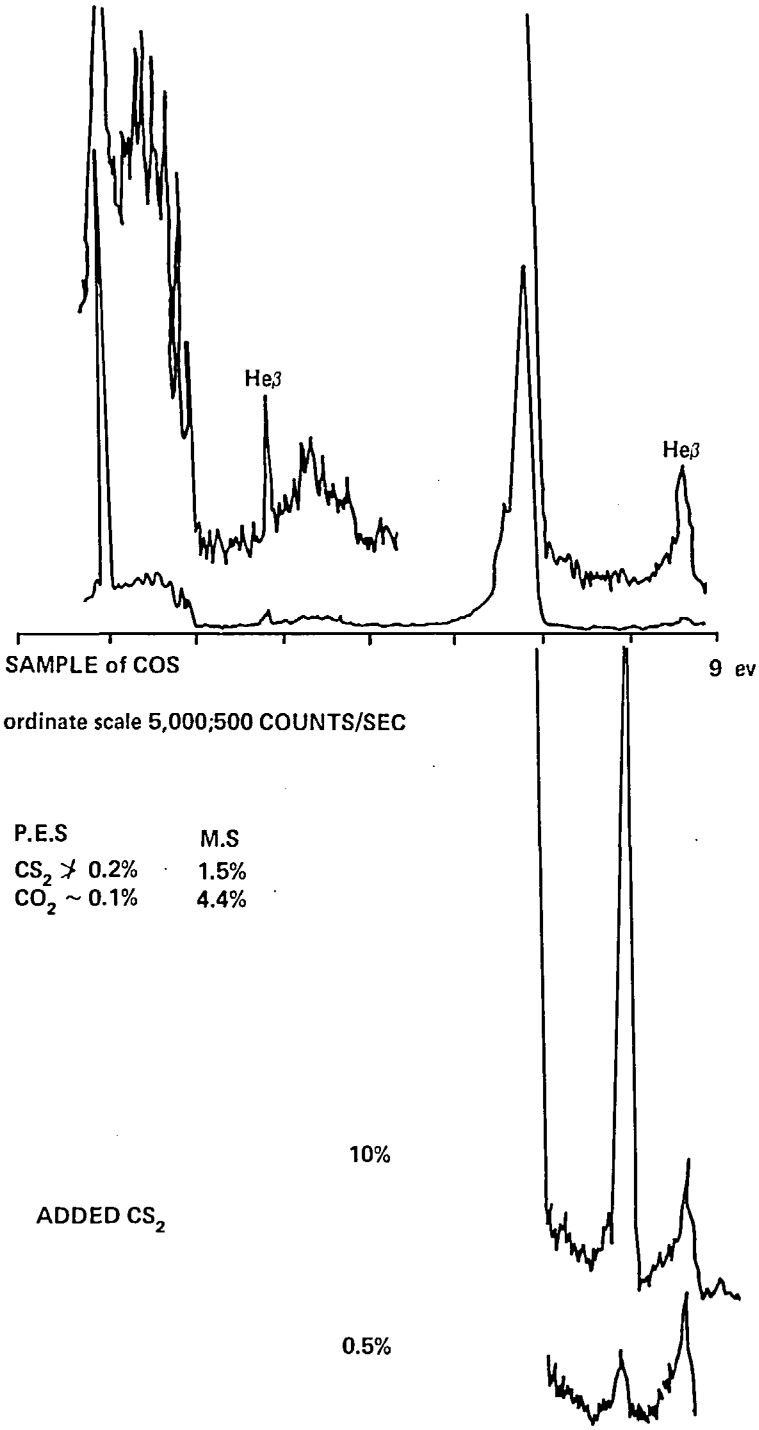


FIGURE 39. Helium(I) photoelectron spectra of a commercial sample of carbon oxysulfide with the addition of known proportions of carbon disulfide. (From Daintith, J., Dinsdale, R., Maier, J. P., Swiegart, D. A., and Turner, D. W., in *Molecular Spectroscopy 1971*, Hepple, P., Ed., Institute of Petroleum, London, 1972, 19. With permission.)

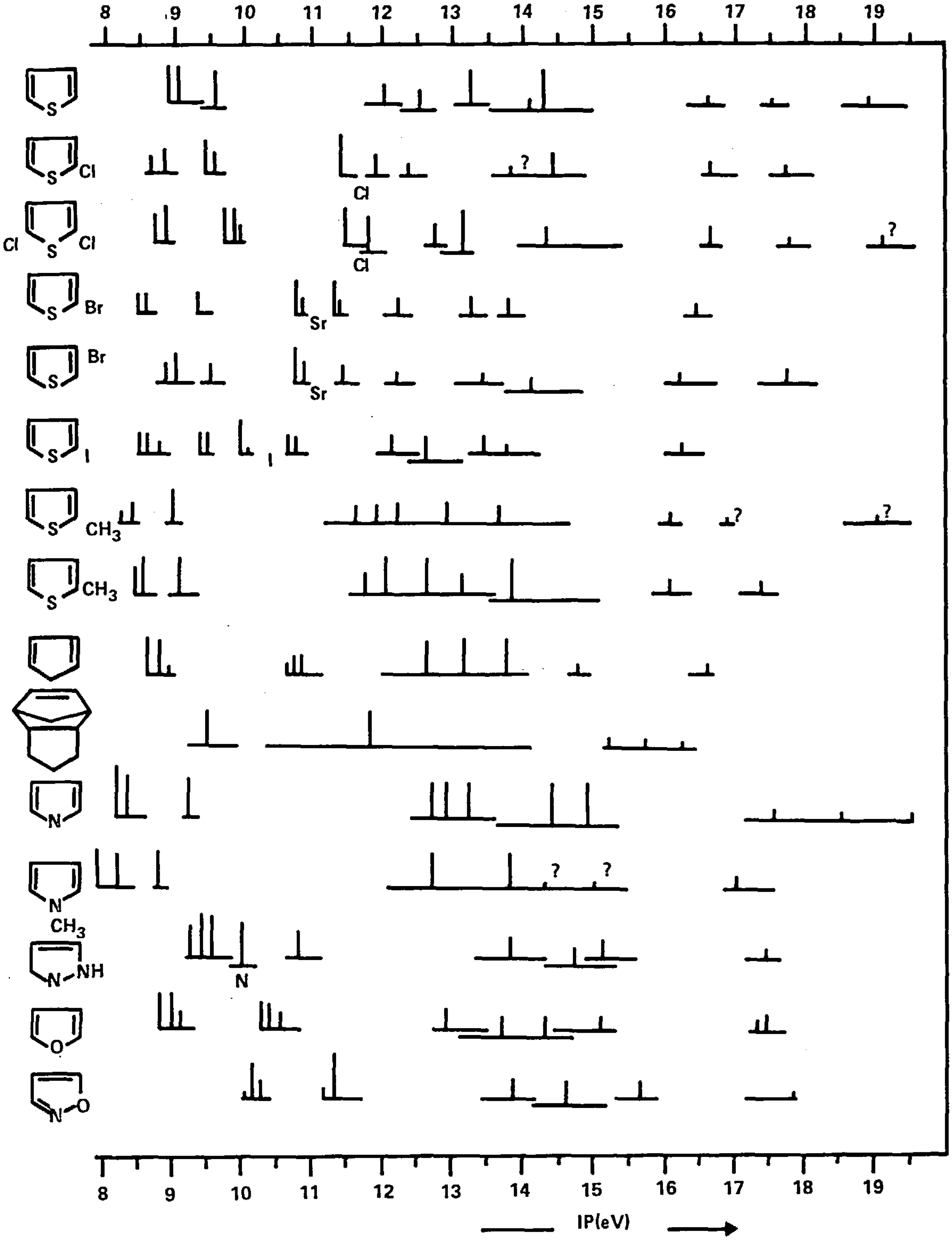


FIGURE 40. Correlation diagram for five-membered heterocyclic compounds. (From Betteridge, D., in *Molecular Spectroscopy 1971*, Hepple, D., Ed., Institute of Petroleum, London, 1972. 83. With permission.)

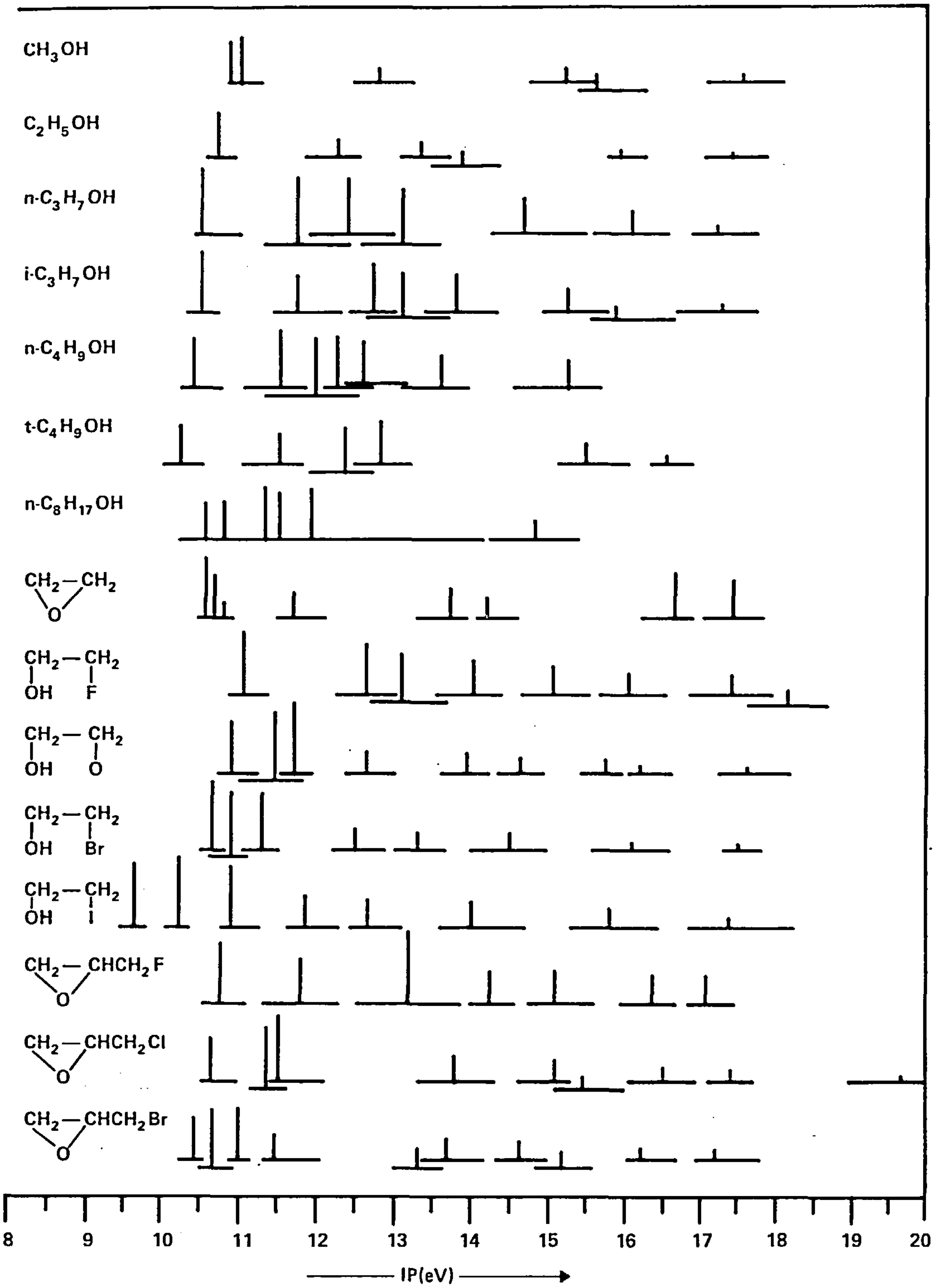


FIGURE 41. Correlation diagram for alcohols and ethylene halohydrins. Each horizontal line represents a line drawn across each spectral band at half its height. Where bands in the spectrum overlay, an extrapolative procedure has been used to estimate half-widths. Thus, overlapping horizontal lines indicate a broad band with clearly defined overlapping components. Vertical lines indicate the positions of peak or band maxima and their height indicates strong, medium, or weak intensity. (From Betteridge, D., in *Molecular Spectroscopy 1971*, Hepple, D., Ed., Institute of Petroleum, London, 1972, 85. With permission.)

easily detect impurities such as CO_2, HCl, H_2O, N_2, etc. Spectrum stripping has been reported to be successful in helping resolve the problem of mixed samples as in the case of PCl_5. The spectrum of "pure" PCl_5 was found to vary with pump-out time of the instrument. When the spectra of HCl and PCl_5 were stripped away, the residual spectrum was that of $POCl_3$, indicating hydrolysis.

Whether the technique can give information of analytical significance not available from other sources is at present not clear. Since the technique is still in its early stages most of the compounds that have been studied are already well characterized, but it seems that there may be areas in which UPS is the technique of choice.

With respect to structure, UPS can give information about the presence of elements such as P, O, S, halogens, N, and metals in volatile complexes. Furthermore, UPS can give some ideas as to the electronic environment about these atoms as reflected by the ionization potentials of their nonbonding electrons, as shown in Figure 42.

As stated above, UPS can distinguish between structural isomerism as in the case of *cis*- and *trans*-dichloropropenes,[13] *cis*- and *trans*-dichloroethylene,[152] 2- and 3-bromothiophene, and 2- and 3-methythiophene.[153] Cheng et al.[163] were able to distinguish between the *ortho, meta,* and *para* toluenenitriles by variations in π_3 line shapes of their UPS spectra. This information could be obtained from other sources, but serves to point out that the technique is sensitive to such effects as *cis* and *trans* isomerism and variations in substitution patterns of cyclic compounds.

UPS can show the existence and extent of interaction of nonbonding orbitals. Wagner and Bock[154] give an account of such interactions in compounds containing S–S linkage. In the case of sulfur this nonbonding interaction can provide data that allow one to distinguish between a S–S linkage that is in a straight chain or cyclic compound. The half width of the "lone-pair" ionization has also been shown to reflect the number of sulfur atoms in the $-(S)_n$ chain for n = 1 to 3[155] (Figure 43).

Using the above features of UPS spectra, Baker et al.[153,156] were able to deduce the presence of halogen substituents adjacent to π systems, identify the individual halogen, infer that the π system was other than benzene, and (through comparison to known spectra) identify the compound in their two-part study of pesticides and related compounds; thus, the potential value of UPS as a method for structural analysis is illustrated.

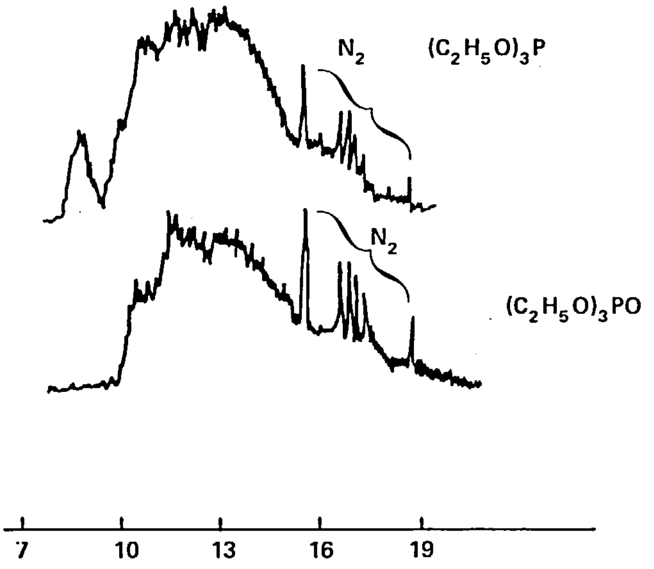


FIGURE 42. UV-PE spectra of triethylphosphite and triethyl phosphate. (Sharp peaks in region 16.5 eV due to nitrogen.) (From Betteridge, D., in *Molecular Spectroscopy 1971*, Hepple, D., Ed., Institute of Petroleum, London, 1972, 89. With permission.)

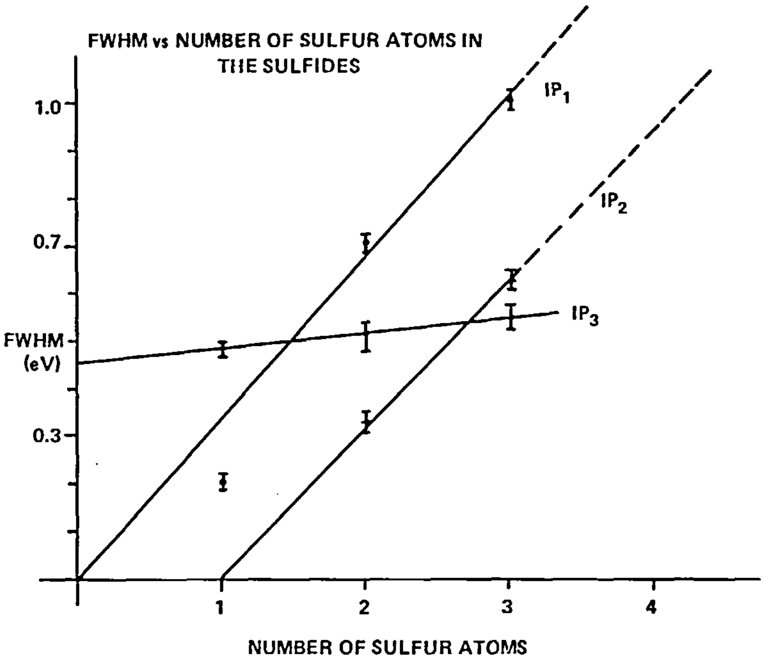


FIGURE 43. Full width at half maximum vs number of S atoms in Me$(S)_n$ Me for first three IP's. IP_3 is primarily S-C and should not change, while IP and IP_2 are associated with S-S and S "long pair" and are a function of the number of sulfur atoms present. (From Prather, J. W., Mallere, P., and Cheng, K. L., results given at 10th Midwest ACS Reg. Meet., November 7, 1974.)

With respect to structural analysis, Meier and Simon[157] have taken an approach by which they were able to correlate ionization potential and substituent effects in substituted aromatics and olefins. The authors found it feasible to assign an increment to individual types of substituents describing their effect on the π_3 bands in benzene. By this incremental approach they were able to correlate IP with substituent to a first order approximation that resulted in the following equation

$$I_{v,exp} = I_{v,calc} = a_0 + \Sigma_j a_j x_j \qquad (8)$$

where

I_v, exp = experimental vertical ionization potential;

I_v, calc = calculated vertical ionization potential;

a_0 = skeleton shift, approx. equal to I_v, exp of benzene;

a_j = shift increment attributed to the jth type of substituent;

x_j = number of times jth substituent is present in the molecule.

Twelve types of substituents were considered (j=1 to 12): $-H$, $-NO_2$, $-CN$, $-C^nF_{2n+1}$, $-CHO$, $-F$, $-Cl$, $-Br$, $-R$, $-OR$, $-OH$, and $-NH_2$. All values were adjusted so that $a_H = 0.0$.

The approximation is crude but the work does show merit when compared to other methods of prediction of ionization potentials. Table 9 shows that in some cases very good results were obtained. Other notable studies along these same lines were given by Cocksey et al.[158] and Masclet et al.[159] The latter paper is comprehensive in its scope, giving data for 63 alkenes.

For olefins it is generally agreed that the first ionization potential is due to removal of a π electron. This IP is related to reactivity of the C=C center with respect to electrophilic reactions[160] and charge transfer complex formation.[161] Thus, it is important to study these types of compound and substituent effects. The authors found several influences on the IP of the π electrons: (a) there is a rapid nonlinear decreasing of the IP with increase in the number of substituents; (b) a dominant effect is the number of carbon atoms in the substituent which expresses the stabilization of the ground state of the ion by all σ electrons of the alkyl groups; (c) a small influence is the relative

TABLE 9

Predicted and Experimental I_V's for Six Compounds Not Included in the Training Set

Compound	Orbital	$I_{v.\,exp}$ (eV)	$I_{v.\,calc}$ (eV)	r (eV)
	π_3	8.6 ± 0.1	8.44	+0.16
	π_3	9.2 ± 0.02	9.08	+0.12
	π_3	9.15 ± 0.02	8.56	+0.59
	π_3	9.2 ± 0.02	9.79	-0.59
	π_3	8.15 ± 0.05	8.08	-0.07
	π_3	8.2/9.25	9.25	-1.05/00
	P_{Cl}	11.0	11.62	-0.62

(From Meier, P. C. and Simon, W., in *Molecular Spectroscopy 1971*, Hepple, P., Ed., Institute of Petroleum, London, 1972, 59. With permission.)

position of the substituents, except where these are numerous (tetrasubstituted alkenes) or very bulky (olefins with *t*-butyl substituents), in which case there is a steric effect superimposed on the preceding effects.

The examples above show the power of UPS in structural studies and are essentially qualitative in nature. By comparison, very few studies with quantitative analysis in mind have been carried out. In fact, only two[149,162] have been reported, both of which were of a preliminary nature. As discussed above, COS samples were analyzed for CO_2 and CS_2 with interesting results. It has also been pointed out that mixtures of compounds present a problem in UPS, and some type of preanalysis separation is in order. A report by Betteridge et al.[162] makes a good attempt at discovering and defining the problems involved with a GLC-UPS interface. The authors tried various methods for sample introduction, a prime factor in sensitivity, and were able to analyze for acetone in water, with the limit on sample size being about 1 μl. Thus, the authors have shown the feasibility of GC-UPS and have made an important step in the progress of UPS as an analytical tool.

B. UPS Studies of Surface

Most surface analyses in electron spectroscopy were done with XPS or AES, since UPS does not provide an atomic identification. UPS, however, is a molecular spectroscopic technique offering detailed valence band structures. Recently, its important role in surface analysis has been gradually realized. A few reports have appeared during the last few years concerning UPS studies of surfaces.[16,22,52]

As shown in Figure 6, Brundle and Roberts[16,22,164] demonstrated the ability of UPS to differentiate between a clean and a dirty Au surface. The authors obtained a limit of detection for adsorbed H_2O on Au as $\sim 5 \times 10^{14}$ molecules cm^{-2}. They stated that in the multilayer region, broadened orbital energy levels may be easily observed with energy shifts with respect to the free molecule values. No vibrational structure is observed with multilayers; measurements of lower coverages are not feasible.[164]

Photoelectron energy spectra and the band structure of the noble metals were studied with the modulated retarding potential technique using a cylindrical geometry.[165] Photoelectron energy distributions and their second derivatatives have been measured on Cu, Au, and Ag in the photon energy range 4.0 to 11.4 eV. Samples were prepared by evaporation in ultrahigh vacuum and were coated with approximately one monolayer of Na or Cs. The spectra obtained show much new structure, lending further support to the interpretation of the photoelectron energy spectra from noble metals in terms of direct transitions in contrast to early work.

UPS energy distributions were reported for noble and transition metals (Ag, Au, Cu, Cr, Ni, Pd, and Ti) over a wide range of photon energies.[52] The results directly show width, positions, and positions of occupied α bands and show nonstationary d-band structure, indicative of direct interband transitions. Theoretical calculations of photoemission energy distributions and optical absorption for Cu show good agreement with the experimental evidence. An application of UPS to gas adsorption studies has been reported (H_2, CO, and O_2 adsorbed on Ti).

UPS technique has been applied to the study of the oxidation of Sr and Cs.[166] By using this technique the photoemission measurement offers a method to determine the oxide growth rate perpendicular to the surface, the composition of the surface, and the stable oxide phases formed during the oxidation process.

An ultrahigh vacuum photoelectron spectrometer capable of measuring electron energy distributions for solids and chemisorbed gases at photon energies of 16.8, 21.2, 26.9, and 40.8 eV has been described.[167] Brundle and Roberts[22] also described a photoelectron spectrometer specifically designed for studying solid surfaces and reactions that occur at these surfaces. This instrument is equipped with both X-ray and UV sources under ultrahigh vacuum conditions. The development and availability of such instruments equipped with UV source certainly facilitates the UPS surface analysis and research. In the past, most UPS work on metals has been limited to photon energies of $6 < h\nu < 11.6$ eV because of work function thresholds (ϕ) and LiF window cutoff (11.6 eV). This energy range has been extended in both directions — to lower energies by cesiation or sodiation to lower the work function, and to higher energies by differentially pumped windowless spectrometers.[52] Further, development in the application of UPS to the surface analysis has included a tendency to use a combined technique including UPS, XPS, AES, and other spectroscopy, as each method has its advantageous features.[16,17]

IV. SUMMARY

Photoelectron Spectroscopy (PES) has emerged 15 to 20 years as a useful method for probing the electronic structure of atoms, molecules, solids, and liquids. Rapid developments in PES are presently occurring, with increasing cross-fertilization and interaction between PES techniques.

Like the emergence of any new technique, the growing number of publications appearing in the journals has been phenomenal. This trend will continue for many years to come before leveling off; however, relatively very little work which applies PES to quantitative elemental or molecular analysis has been done so far. In the past several years ground has been laid for future advancement of quantitative chemical analysis by PES. Both UPS and XPS are basically techniques for trace substances and surface analysis. They demand a clean sample surface and an ultrahigh vacuum. When the PES instruments are available commercially, more analytical applications of UPS or XPS to trace analysis and oxidation states determination are expected. At the present, He(I) and He(II) for UPS and Al (Kα) and Mg (Kα) for XPS are the common radiation sources for PES. Synchrotron radiation has been used for excitation as a continuously variable wavelength source in PES. Such a source has several advantages which are of particular interest in PES. It allows the detailed analyses of photoelectron cross sections for different subshells. This information can then be used in the theoretical treatment of molecular systems on an LCAO basis, for instance, implementing the intensity model on the valence electron spectrum of a molecule.[15]

Sensitivity and resolution of UPS and XPS spectra can be further increased by improving the instrumentation. Siegbahn[15] improved the quality of spectra with his newly designed "prototype" XPS instrument. He claimed that the better resolution for the lower spectrum in Figure 44 was due to the use of monochromatic AlK_{α} radiation source; but, it could be due to careful sample handling and a simple means of equalizing the charges on the surfaces of insulating samples. The introduction of the chevron plate (in conjunction with a resistive strip) and Vidicon has improved the electron counting efficiency.

Applications of angular dependence of either an exciting radiation source to the surface or an electron ejected from the surface will increase or decrease the intensities of spectral lines for certain atoms and molecules. This results in the improved sensitivity and selectivity of PES spectral capabilities. More work on better characterization of surfaces with angular distribution of photoelectrons may be anticipated.

In recent years more attention has been given to the importance of satellite structures which may help the interpretation of photoelectron spectra and their applications in trace analysis. The satellite peaks may be complex and show chemical shifts like the main peaks. Brand and Freiser[169] compared the XPS spectra of so-called secondary Cu(II) dithizonate and other compounds of Cu(I) and Cu(II), with their conclusion that the 1:1

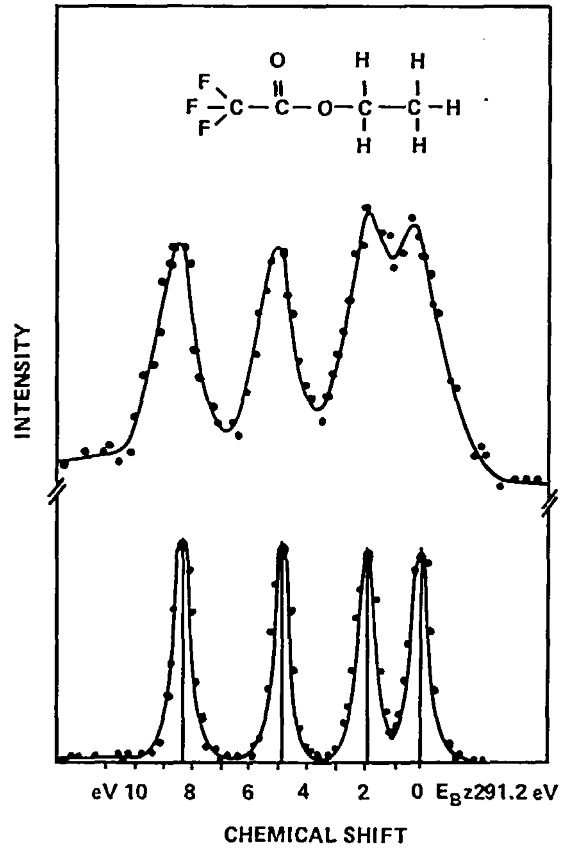


FIGURE 44. The XPS shifts of the C 1s in ethyl trifluoroacetate. Upper spectrum from the early instrument and lower from the newly designed "prototype" instrument. (From Siegbahn, K., Electron Spectroscopy – An Outlook, UUIP-880, Institute of Physics, Uppsala University, August 1974.)

complex formed from the reaction of excess Cu(II) and dithizone is a Cu(I) complex. Furthermore, the XPS spectra of paramagnetic Cu(II) complexes exhibit the characteristic "shake-up peaks" (those of Cu(II) acetate, a diamagnetic dimer) as well as those of the bona fide Cu(I) dithizonate and the so-called enol do not.

When an electron leaves a molecule the remaining electrons will relax and the molecules adopt slightly changed interatomic distances. This can cause vibrational structure not only in the valence band but also in the core lines. The intensities of the shake-up lines appearing on the low kinetic energy side of the main peaks are directly related to the relaxation or shrinkage of the remaining ion-electron system. For an atom the relaxation energy, which is a measure of the shrinkage, for the various shells can be calculated. More recent calculations on these relaxation (or reorganization) energies for ionization in various shells and for all elements between H to Cu have been made by Gelius et al.[4] The discussion regarding the details of the relaxation process for molecules and metals is presently, in part, somewhat esoteric.[15] However, recent work on relaxation phenomena has been reviewed by Shirley in an attempt to unify the work done up to date in this area.[171]

The PES technique is still at a rudimentary stage and less well-developed than the high-efficiency spectroscopic techniques such as mass spectroscopy and NMR. PES will become an instrument equally as important as MS or NMR in the chemical laboratories in the not too distant future. Mass spectroscopy was not a very important analytical instrument before the introduction of the GC/MS combination. In a similar way one would expect the combination of UPS, XPS, AES, and others as powerful analytical tools. The combination of chromatography and photoelectron spectroscopy (for example, GC/PES) deserves our immediate attention and efforts for promoting new horizons of analytical spectroscopy.

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