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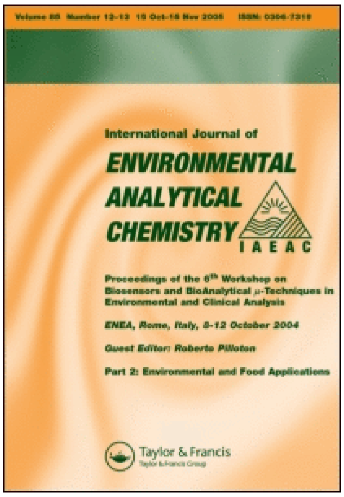

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Electron Spectroscopy - A Potentially Useful Tool for Environmental Studies

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Electron Spectroscopy— A Potentially Useful Tool for Environmental Studies†

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The technique of electron spectroscopy (ESCA) is reviewed. Those aspects are discussed which seem to be of greatest potential interest to workers in environmental studies. Basic theory of the photoelectron ejection process is considered along with the Auger effect. Factors affecting the calculation of electron binding energies are discussed. Instrumentation utilizing both magnetic and electrostatic monochromators is discussed in some detail.

The nature of ESCA data is considered, along with an extensive tabulation of chemical shifts observed for 15 elements. Application of ESCA to surface studies is reviewed, using examples like effect of layers of material on electron intensities, investigations of zeolites and some elementary catalysis studies. A review of the quantitative aspects of ESCA considers the determination of arsenic in soils and the measurement of mixed oxide ratios.

INTRODUCTION

Electron spectroscopy is a relatively new chemical tool which is proving to be of great use to analytical chemists. Although quantitative calculations of binding energies are not yet possible, on an empirical basis much information may be obtained in a manner similar to that employed in NMR or infrared spectroscopy.

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The original papers describing electron spectroscopy were published by Siegbahn *et al.*[1] and Turner,[2] both of whom developed the technique for studying ionization potentials. The principle involved is fairly simple and straightforward. If an atom or a molecule is bombarded with radiation of sufficient energy, an electron may be excited to the free electron level and thus be ejected. The difference between the energy of the exciting radiation and the binding energy appears as kinetic energy of the electron. If this quantity is determined, one can easily calculate the binding energy or ionization potential of the ejected electron.

The type of electron which may be ejected depends upon the energy of the exciting radiation. One may study valence shell electrons using vacuum UV photons, while core electron ejection is possible only with radiation of much higher energy, such as x-rays. Photoelectron Spectroscopy (PES) refers to the use of UV photons in electron excitation and ESCA or Electron Spectroscopy for Chemical Analysis, the method to be discussed here, refers to the use of x-rays.

The binding energies of core electrons are affected by the chemical environment of the atom in a manner to be discussed below. Electron spectroscopy, in measuring the binding energies, thus provides a useful tool for probing the inner electrons for information concerning bonding and molecular structure. In a manner similar to that provided by IR, empirical correlations make qualitative analysis a possibility. In addition, since the electron beam intensity is proportioned to the number of similar atoms in the sample, the technique also becomes useful in quantitative analysis.

The present paper will emphasize two aspects of ESCA, namely, its use in studies characterizing the nature of surfaces, and the quantitative aspects of the technique. Although ESCA must undergo considerable development prior to application to environmental studies, it appears to offer great promise for fundamental air and water pollution studies. A recent paper has reviewed fundamental aspects and instrumentation in greater detail than can be presented here.[3]

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THEORY

When an atom or molecule is bombarded with x-rays of sufficient energy, a core electron may be ejected. The probability of any given electron's being excited to the free electron level is in general inversely proportional to the square of its orbital radius and directly proportional to the cube of the atomic nuclear charge (Z). The atom, left with a positive hole in an inner orbital, is an excited ion which then relaxes by an outer shell electron dropping to fill the vacancy. The energy released in the process may appear in one of two ways—

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a photon may be emitted via x-ray fluorescence, or yet another electron, termed an Auger electron, may be ejected. The two processes are competitive in the electronic relaxation process. Whereas the kinetic energy of the initial photoejected electron is dependent upon the energy of the exciting radiation, that of the Auger electron is not, since it represents the energy difference between the initial and final states of the ion.

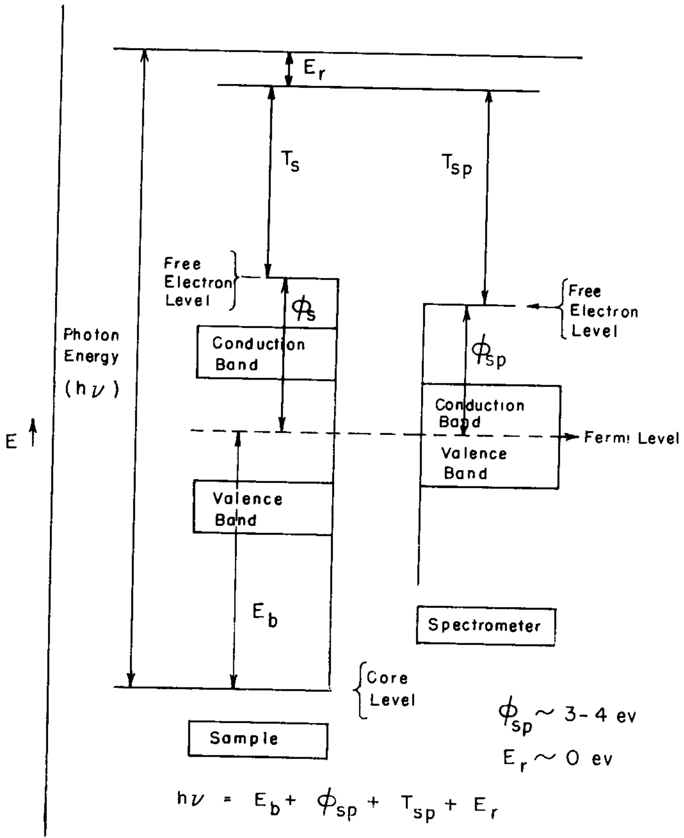

FIGURE 1 Binding Energy Scheme for Sample and Electron Spectrometer.[3]

h_ν = Energy of exciting photon
E_b = Binding energy of photoejected electron
ϕ_s = Sample work function
ϕ_{sp} = Spectrometer work function
T_s = Kinetic energy of electron photoejected from the sample
T_{sp} = Kinetic energy of the electron measured by the spectrometer
E_r = Recoil energy

It is the primary, photoejected electron whose energy is the key to binding energy calculations; however, the constancy of the Auger electron energy provides a good internal standard, at times, in electron spectroscopy.

In the electron spectrometer the exciting radiation is produced at a cooled cathode usually composed of aluminium or magnesium. The resulting x-rays are directed onto the sample which is coated as a thin layer onto a metal mesh or tape in the sample compartment. The electrons which are ejected enter the monochromator and are dispersed according to energy. As the magnetic or electrostatic field is either increased or decreased, electron beams of varying energies are focused on the counter. The intensity of the electron beam is recorded as a function of energy as the field is scanned.

In Figure 1 the relationships among the energies of the processes involved in the calculation of binding energies are illustrated. The energy levels of the sample, assumed to be an electrical insulator, are depicted in the center. The sample Fermi level is taken to be midway between the valence and conduction bands. The spectrometer is assumed to be a conductor with a Fermi level, by definition, at the boundary between the valence and conduction bands. When two materials are in electrical contact, their Fermi levels are assumed to be at a common level; the sample and spectrometer levels, therefore, are so placed relative to one another. The energy of the exciting photon, depicted at the left, is distributed among four processes. To raise the electron from its core level to the Fermi level requires an energy termed the binding energy E_b, the parameter sought by ESCA. From the Fermi level to the free electron level, the energy is denoted ϕ_s or the work function in the sample. The energy left over is divided between the kinetic energy of the electron T_s and the recoil energy, E_r, which arises from consideration of conservation of momentum.

In traveling from the sample to the slit, the electron is accelerated or decelerated as it experiences a potential due to the difference in work functions of the sample ϕ_s and the spectrometer ϕ_{sp}. As it reaches the free electron level of the spectrometer, it attains a kinetic energy T_{sp}. Fortuitously the recoil energy has been shown[1] to be negligible. The binding energy can then be calculated from the equation

$$E_b = h_v - \phi_{sp} - T_{sp}.$$

To calculate absolute binding energies accurately, one must know the work function of the spectrometer. But if only relative measurements are necessary, ϕ_{sp} may be assumed to be constant.[1]

Since electron spectroscopy, x-ray absorption, and x-ray fluorescence involve the same phenomena, the same information might be assumed to be obtainable from all three. Although this is true, the binding energies are more easily derived from ESCA data. Line widths of photoejected electron energies

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are in general much narrower than fluorescence lines and easier to interpret than absorption edges. Also, x-ray fluorescence arises from relaxation of excited ions, giving only minimal chemical shifts.

INSTRUMENTATION

An electron spectrometer contains the following five basic components: (1) the source of the ionizing radiation, (2) the sample compartment, (3) the monochromator for dispersing the electron beam into its component energies, (4) the detector, which produces a measurable response proportional to the intensity of an electron beam, and (5) the scanning and readout system. A block diagram of a typical ESCA system is shown in Figure 2. Depending on the specific source, monochromator and detector chosen, one can design an electron spectrometer for various specific purposes. However, only those components which are of use in ESCA particularly will be discussed here.

Currently there are five instrument companies manufacturing and distributing electron spectrometers. All utilize electrostatic monochromators. These companies are AEI, Hewlett-Packard, McPherson, Varian and Veeco.

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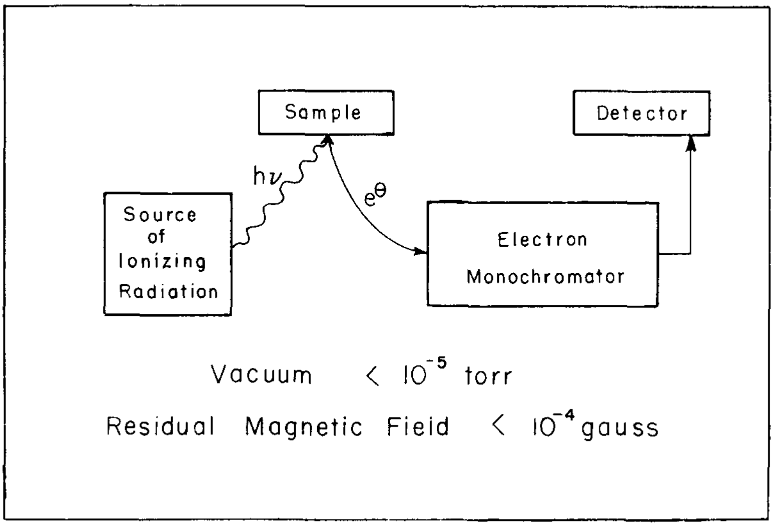

FIGURE 2 Block Diagram of the Essential Elements of an Electron Spectrometer.[3]

Sources

The x-ray tubes which are used in ESCA utilize a heated cathode at a high negative potential and a water-cooled anode composed more frequently of aluminum or magnesium. The high power dissipated necessitates cooling. In order to minimize localized heating of the anode surface, a rotating anode system has been used. The most frequently used x-rays are the Al and Mg K_α lines since they produce narrow intense lines which are capable of ejecting core electrons in most elements of interest. Also, in order to minimize tungsten deposition from the filament on the anode, the geometry of the source should be such that the anode is not in a direct line with the cathode.

In order to reduce the background signal caused by scattered electrons from the source entering the sample chamber, a thin window of aluminum separates the two compartments. The Al K_α x-rays pass through to the sample while the scattered electrons do not. A bent crystal monochromator, as used in the Hewlett-Packard instrument, can be used to select monochromatic x-rays for excitation, but intensity of the exciting radiation must be sacrificed to do so.

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Sample

Because the sample compartment must be evacuated to about 10^{-5} Torr or below, a practical restriction on the sample must be that it have a low vapor pressure. Cryogenic probes may be used to run samples which are volatile at room temperature. If differential pumping techniques are employed, gaseous samples may also be analyzed. In freezing the sample, it must be ensured that the freezing process does not significantly affect the resulting data. Another restriction on the sample is that it not decompose under the high vacuum.

The photoejected electrons which reach the monochromator emerge from a depth in the sample of not more than 100 Å, making ESCA a particularly good surface technique. However, if bulk properties are sought, one must be sure that the data obtained from the surface are representative of the bulk properties.

Electron spectroscopy is an extremely sensitive technique requiring very small samples—on the order of micrograms. The sample must be in good contact with electrical ground to eliminate the possible effects of sample charging.

Monochromators

In the monochromator the electrons are dispersed according to their energy and a small portion of the spectrum is focused on the detector or counter. Two basic methods, magnetic and electrostatic, are used to perform this function.

The magnetic instrument, a donut shaped apparatus with a radius of 30 cm, is adapted from the design of Siegbahn *et al.*[1] It uses an inhomogeneous magnetic field produced by a set of four cylindrical coils placed around the electron trajectory, to provide double focusing, as shown in Figure 3(*a*).

Since it is necessary to resolve the electron energies to within 0.1 %, it is essential to maintain fluctuations in the magnetic field which focuses the electrons to a similar value. The instrument must be iron free and all extraneous fields including the earth's field must be reduced to essentially zero within the instrument. A series of Helmholtz coils provides magnetic compensation for most such instruments.[4]

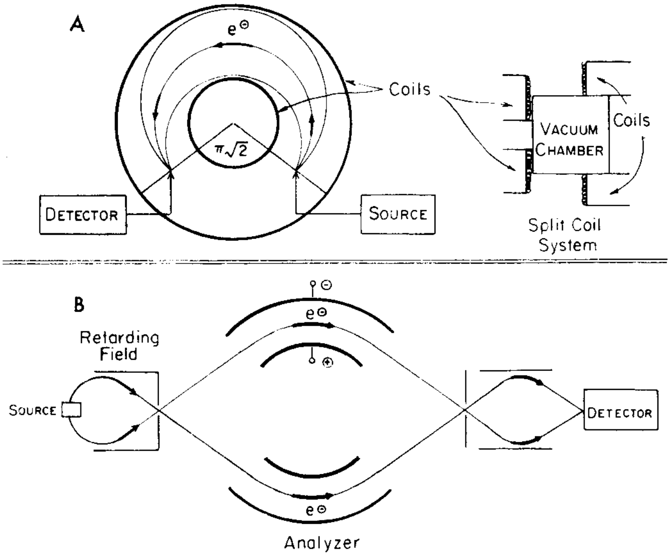

FIGURE 3 Schematic Diagrams of Magnetic and Electrostatic Electron Monochromators.[3]

A. Double focusing magnetic spectrometer. The view to the right is a vertical cross-section.

B. Electrostatic spectrometer using a spherical analyzer and retarding field.

Paramagnetic materials such as μ-metal, Netic and Conetic shielding, while not applicable for the magnetic instrument, are useful for shielding an electrostatic monochromator. Helmer and Weichert[5] describe an electrostatic monochromator consisting of two concentric spheres with a potential difference between them. A retarding field reducing the electron energy by a factor of 10, permits the use of a relatively small monochromator. Such a design is shown in Figure 3(*b*).

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Detectors

Of the three types of electron counters which have been used in the development of ESCA, only the electron multiplier is currently in use because of its superior characteristics and convenience. Sensitive to even low energy electrons, its output is fed into a charge sensitive amplifier and then into a rate meter or scalar. For a discussion of GM counters and photographic plates, refer to Siegbahn *et al.*[1]

Scan and Readout System

Three general methods of scanning the spectrum of electron energies, providing an intensity vs. energy plot, may be used. The continuous scan method sweeps the entire energy range once, linearly varying the field as a function of time. The intensity of the beam is recorded instantaneously as a function of the field or the electron energy.

The incremental scan technique divides the spectrum into a large number of finite increments. Either manually or automatically by computer, each successive increment is focused on the detector and the signal counted and recorded. A television unit connected with the computer permits continuous monitoring of the spectrum.

The multichannel approach compensates for a problem inherent in both the continuous and incremental scan techniques. Instead of scanning incrementally a single time using relatively long counting periods at each increment, each increment is counted for a short time and the signal recorded. The energy range is rescanned many times and the successive signals for each increment are summed until sufficient data are obtained. Any fluctuations in the source as a function of time are therefore felt by all parts of the spectrum equally instead of by just a few channels.

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NATURE OF ESCA DATA

The core electrons, which are studied by ESCA, experience from the positively charged nucleus an attractive force which is known as the binding energy. The presence of the outer, valence shell electrons somewhat reduces or screens this attractive force. However, if the atom loses a valence shell electron, becoming more positively charged, some of the screening is removed and the binding energy of the core electron is effectively increased. Within a given atom, it can be seen that, as an atom takes on a more positive charge, the binding energies of its core electrons increase; conversely, as it takes on a more negative charge, the binding energies decrease.

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TABLE I

Representative ESCA Chemical Shifts[a]

Oxidation State[b]

Element[c]	−3	−2	−1	0	+1	+2	+3	+4	+5	+6	+7	Ref.
[5] Boron (1s)	—	—	—	0	—	—	+5.7	—	—	—	—	(6)
[7] Nitrogen (1s)	—	—	0[e]	—	+4.5[d]	—	+5.1	—	+8.0	—	—	(7)
[17] Silicon (2p)	—	—	—	0	—	—	—	+4	—	—	—	(8)
[15] Phosphorus (2p)	−1.3	—	—	0	—	—	+2.8	—	+3.1	—	—	(9)
[16] Sulfur (2p)	—	−2.0	—	0	—	—	—	+4.5	—	+5.8	—	(1)
[17] Chlorine (2p)	—	—	0	—	—	—	+3.8	—	+7.1	—	+9.5	(10)
[24] Chromium (3p)	—	—	—	0	—	—	+2.2	—	—	+5.5	—	(6)
[29] Copper (1s)	—	—	—	0	+0.7	+4.4	—	—	—	—	—	(11)
[33] Arsenic (3d)	0	—	—	—	—	—	+3.9	—	+5.3	—	—	(10)
[34] Selenium (3p)	—	−1.0	—	0	—	—	—	+3.6	—	+4.5	—	(12)
[35] Bromine (3d)	—	—	0	—	—	—	—	—	+6.0	—	+7.6	(13)
[42] Molybdenum (3d)	—	—	—	0	—	—	—	+4.3	—	+6.0	—	(14)
[52] Tellurium (3d)	—	−0.7	—	0	—	—	—	+2.4	—	+3.5	—	(12)
[53] Iodine (4s)	—	—	0	—	—	—	—	—	+5.3	—	+6.5	(15)
[63] Europium (4p)	—	—	—	0	—	—	—	+7.8	—	—	—	(16)

[a] All shifts in electron volts. Measured relative to the oxidation state given as zero.

[b] These are formal oxidation states given for the elements indicated. They indicate the approximate magnitude of chemical shifts for an element in a given state. The actual values will vary, depending on counterion and nearest neighbor atoms.

[c] The atomic number is given in brackets [ ] to the left of the element and the electrons measured in parentheses ( ) to the right.

[d] End nitrogen in NaN_3.

[e] Middle nitrogen in NaN_3.

Binding energy data thus provide information concerning the electron density about a particular atom and therefore tell much about its chemical environment. Changes in the peak position relative to some reference are known as chemical shifts.

Table I illustrates representative chemical shifts for the elements investigated to date. These shifts have been calculated for specific compounds and therefore are not measures of the exact shift to be expected for a given

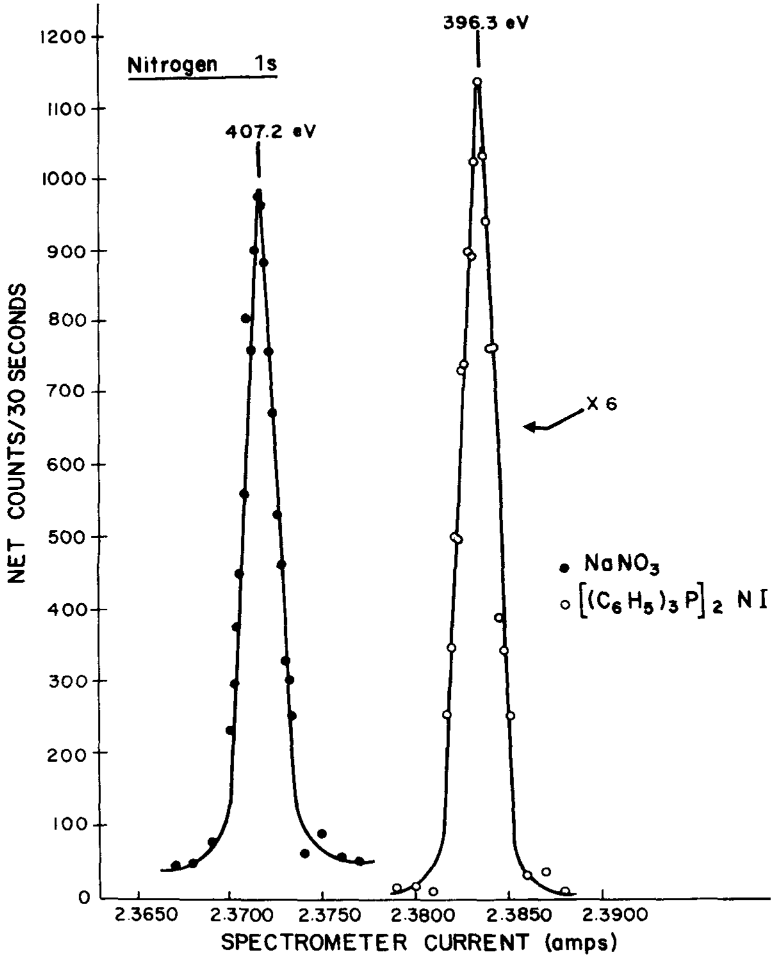

FIGURE 4 Nitrogen 1s Electron Spectra for Sodium Nitrate (—●—●—●—) and Bis-(triphenylphosphine)-iminium Iodide (—○—○—○—). Spectra obtained on a double-focusing magnetic spectrometer of the split coil type.[20]

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element. These shifts will be modified depending on the counter ion present as well as the exact molecular geometry in the vicinity of the atom investigated.

If the binding energy of a given electron is increased by a decrease in electron density as in the oxidation of Cu^0 to Cu^{+2}, the kinetic energy of the ejected electron on the detector then becomes smaller, shifting the peak to a lower field.

Many approaches have been tried in an attempt to correlate quantitatively the experimentally observed chemical shifts with calculated binding energies or electron densities. To date the molecular orbital approach has met with the most success, although the agreement is still only qualitative.

Fortunately the use of ESCA as an analytical tool does not depend upon the ability to predict binding energies from first principles; empirical data and correlations provide sufficient information for the technique to be used successfully both in qualitative and a quantitative analyses and in structure determinations. Data are being collected and compiled into empirical correlation charts[3] which may be used, at least partially, in the same manner as the Colthup charts in IR analysis. Peak intensities, on the other hand, are easily related to quantitative analysis.

Figure 4 illustrates the electron spectrum of the nitrogen atoms in two different molecules, sodium nitrate and bis-(triphenylphosphine)-iminium iodide. (PPN^+I^-) The nitrogen 1s binding energy in the PPN cation is less than that in $NaNO_3$ by 10.9 eV indicating that the PPN nitrogen carries more of a negative charge than the nitrate nitrogen. The peak widths at half-height for the N (1s) electrons are in general about 1.8 eV.

In a slightly different type of spectrum, that of MoO_3, shown in Figure 5, the splitting of the 3d ($3d\frac{3}{2}$–$3d\frac{5}{2}$) electron energies in the molybdenum may be observed. The two peaks are completely resolved at a separation of only 3.1 eV. The relative intensities, or the peak areas, correspond to the relative probability of ejecting those particular electrons. The peak widths at half-height for MoO_3 were ca 1.7 eV.

Figure 6 represents the electron spectrum of an elemental tellurium sample taken after it was exposed to the atmosphere for several months. A doublet is observed for each tellurium species, corresponding to the $3d\frac{3}{2}$–$3d\frac{5}{2}$ electron doublet. The same sample, when fresh, exhibited the 582.0 eV and 572.0 eV peaks at much greater intensity relative to the smaller peaks, indicating that the two less intense peaks correspond to the oxidized Te(VI) species which increased with exposure to the atmosphere. As in the molybdenum spectrum, the peak areas of the Te^0 doublet or of the Te(IV) doublet correspond to the relative probabilities of ejecting the given electrons. The heights of the Te^0 peaks relative to those of the Te(IV) species are indicative, in fixed samples such as this, of the relative proportions of each species on the sample surface.

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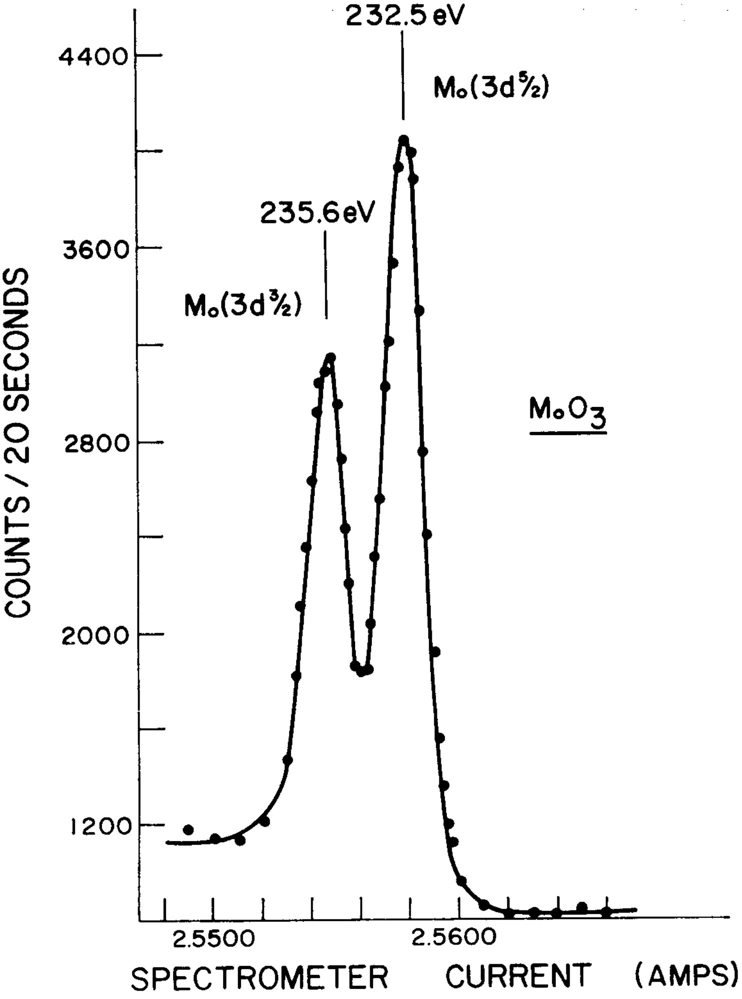

FIGURE 5 Molybdenum 3d$\frac{3}{2}$–3d$\frac{5}{2}$ Electron Spectrum for MoO_3.[14] Spectra obtained on a double-focusing magnetic spectrometer of the split coil type.[20]

Surface Studies

Electron spectroscopy has proven to be of particular value in surface studies since the photoejected electrons in general actually represent molecules which lie within a few molecular layers of the surface. The mean escape depth of an electron, however, is not constant, but is dependent upon the kinetic energy of the electron and the atomic number of the material, low Z materials being more permeable than high Z materials. It becomes important in doing

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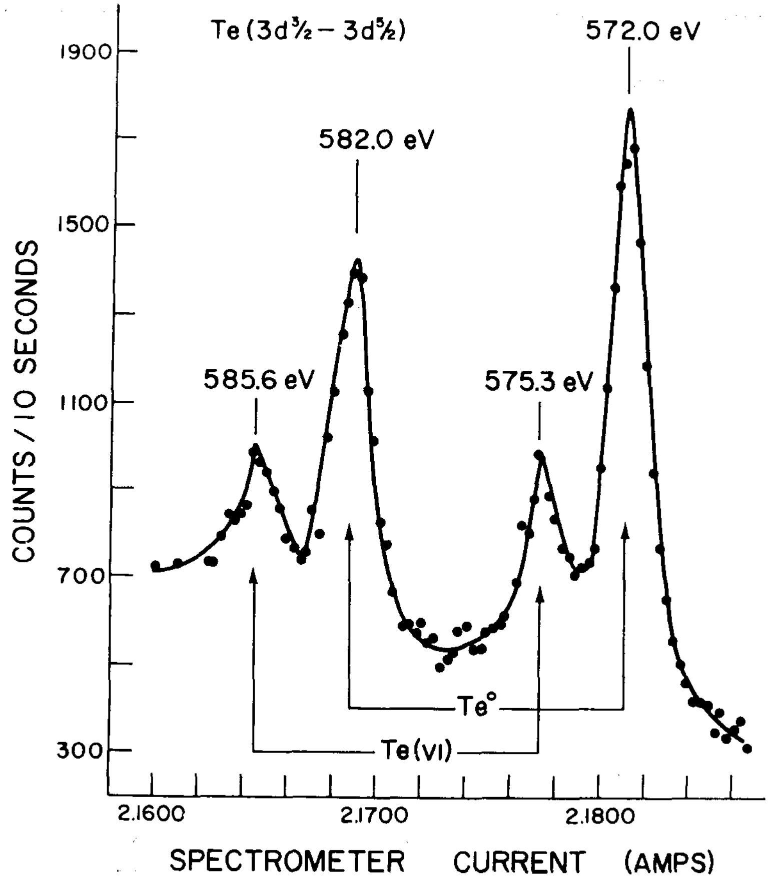

FIGURE 6 Tellurium $3d\frac{3}{2}$–$3d\frac{5}{2}$ Electron Spectrum for an Elemental Tellurium Sample Exposed to the Atmosphere.[12]

The 585.6 eV and 575.3 eV peaks are due to Te (+4).

The 582.0 eV and 572.0 eV peaks are due to Te^0.

Spectra obtained on a double-focusing magnetic spectrometer of the split coil type.[20]

studies of surface phenomena to know which level in the sample is represented by the photoejected electron peak. A discussion of the point is presented by Delgas, Hughes and Fadley[17] in which data for iodostearic acid[1] are compared with data obtained for silver.[18] The experiments by Siegbahn involved the deposition of layers of α-iodostearic acid on a metallic slide. The intensities of the iodine $3d\frac{5}{2}$ peaks were compared from samples containing one, three and ten molecular double layers. The counting rate did not increase proportionally; the intensity from a sample of ten double layers being only 3.5 times that from one of a single layer. Calculations indicated that the photoejected electrons emerged from an average depth of less than 100 Å.

Another experiment discussed by Siegbahn *et al.*[1] involved the deposition of 200 molecular layers of α-bromostearic acid on 2 chromium plated brass slides. One of the slides was, in addition, coated with two layers of stearic acid not containing bromine. The fact that no chromium peaks were observed indicates that the 8000 Å of organic material provided complete shielding for the metal. The bromine signals were observed in both samples, although the carbon-to-bromine peak ratio was smaller in the sample which contained the extra layers of stearic acid.

Electron spectroscopy may therefore be employed in studies of surface layers of material from a monolayer, which produces an easily measurable signal, to a depth which depends upon the material and the electron energy.

One such study[19] concerns the reduction of an iron oxide surface on an iron foil. The reduced iron beneath the oxide layer produced a visible peak at a slightly lower binding energy or higher kinetic energy than that of the surface oxidized iron. The oxygen 1s signal was monitored in addition to the Fe (3p) peaks as the foil was exposed to a flow of H_2 at 10^{-2} torr and increased temperatures. The oxidized iron peak disappeared as did the oxygen 1s peak as the temperature was raised, while the Fe^0 signal at lower binding energy increased.

An example of the use of ESCA in surface adsorption studies is discussed in the article by Delgass, *et al.*[17] Spectra were taken of a NH_4^+ exchanged Y-zeolite wafer subjected to various conditions and the nitrogen containing surface adsorbed layer was studied. The intensity of the nitrogen (1s) peak decreased by more than half when an 85% NH_4^+ exchanged wafer was exposed to heat and vacuum treatment, indicating desorption under those conditions. Exposing the above wafer after desorption to 5 torr of pyridine produced an additional peak on the electron spectrum, displaced from the ammonium induced peak to a higher spectrometer current and therefore lower binding energy. The shift between the NH_4^+ peak and the additional peak following pyridine exposure is similar in magnitude to that observed for the shift between the N (1s) lines in the NH_4^+ of NH_4NO_3 and in pure pyridine, giving added creditability to the assignment of the pyridine peak.

Catalysis by active metals is in general a surface phenomenon and therefore, to improve efficiency, the metal is often plated or dispersed in a thin layer on a support. Electron spectroscopy offers a method of studying reactions and bonding taking place on these metalic surface layers. Changes in oxidation state and chemical composition are easily discernible by ESCA.

Several such studies are reported by Delgass *et al.*[17] One investigation involved the comparison of the Pt ($4f\frac{5}{2}$–$4f\frac{7}{2}$) electron binding energies in

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different forms of the metal in a finely divided form, as a foil, as an oxide, and on a SiO_2 support. The SiO_2 support wafer was coated with Pt and subjected to varying conditions of temperature and atmosphere. The electron spectra were then used to study the effects of these conditions on the oxidation state of the platinum.

Copper also was studied as a 5% layer on a MgO support. MgO was impregnated with a solution of cupric acetate in ethanol and was, for some spectra, calcined at 1000°C in air in an attempt to form a Cu/MgO solid solution. Comparison of the Cu ($2p\frac{3}{2}$) peaks from samples which were dried and those exposed to the oxidizing treatment led to some speculations concerning the species present in each case. Exposure of a copper acetate/MgO wafer to 500° at low H_2 pressure gave rise to a spectrum in which the copper peak was shifted predictably to lower binding energy and was considerably narrowed. Prereduction of a wafer produced a copper peak at yet lower energy indicating even more reduction of the metal. The fact that Cu peaks from both reduced wafers were at lower binding energies than that from a copper foil sample could readily arise from sample charging effects.

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A more straightforward example of a surface study involving a supported metal is discussed in the same publication. The nickel ($2p\frac{3}{2}$) lines were studied in samples containing nickel in various forms. Spectra of black N_2O and a Ni foil stored in the atmosphere exhibited two common peaks; the foil sample contained in addition a small shoulder at lower binding energy. Sanding of the foil practically eliminated the peaks common to the NiO spectrum while enhancing the shoulder. A spectrum of a polished single crystal of Ni showed a spectrum containing the same peaks as the sanded foil. An explanation of the spectra is relatively uncomplicated. The foil initially was coated with a layer of the oxide which was almost completely removed during the sanding, exposing fresh metallic nickel.

Although the reason for the existence of a doublet in the NiO spectrum is not completely clear, the positions of the peaks may be taken as a "fingerprint" of the species. A spectrum of a silica-aluminum support wafer impregnated with $Ni(NO_3)_2$ and calcined in air at 760°C showed peaks resembling those of NiO indicating that the Ni on the support was largely NiO. Treatment of the same wafer with a reducing atmosphere gave rise to a spectrum containing a peak in the free Ni^0 position.

Sulfidation of a supported Ni sample produced a doublet nickel spectrum, the splitting of which was not similar to that of NiO.

Quantitative Analysis

Electron spectra of widely different compounds as reported by Siegbahn[1] demonstrate the sensitivity of ESCA and its potential use in quantitative

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analyses. Experiments were conducted, for example, on a monomolecular layer of iodostearic acid. Although the amount of iodine was extremely small, on the order of thousandths of a microgram, a strong iodine signal was observed.

In another compound, vitamin B_{12}, cobalt is present as a very small fraction of the large molecule. Yet the cobalt peaks could be easily distinguished in a 100 Å thick layer of the vitamin and its chemical environment studied. The sulfur atoms, numbering one for every 140 other atoms, could also be observed and their oxidation state determined. Such information can be of great value in the investigation of biochemical processes, the oxidation states of central atoms being of importance, many remaining yet unknown.

As mentioned previously, a broad sweep of the electron spectrum provides a method of qualitative analysis by means of peak positions. However, the peak intensities, which are proportional to the number of similar atoms in the sample, offer a convenient quantitative method. After correcting the peak height for various effects, i.e. variation in photoelectric cross-section, attenuation of electrons emerging from the sample, and detector efficiency, good agreement was found between relative heights and stoichiometric formulae.[1] Spectra of various amino acids illustrate the application of this technique to biochemical analysis.[1]

Evidence against the existence in "polywater" of a unique form of polymerized water has been corroborated by an ESCA investigation reported by Davis *et al.*[19] Samples of the "polywater" prepared in the prescribed manner were placed on pure gold support discs whose background spectra were recorded. Simultaneous analysis of the samples by infrared confirmed that they were indeed similar to those already reported.

Because ESCA is sensitive to all elements but hydrogen, a complete scan of the electron spectrum yields an elemental analysis of the sample. Such scans of "polywater" preparations from various different sources showed that all contained similar contaminants—sodium and potassium salts of sulfate, chloride, nitrate, borates, silicates, and carbon-oxygen compounds. Almost the entire spectrum could be identified without assuming the presence of the anomolous polymerized water. The authors concluded that it is likely that the reported unique properties of polywater are due, not to a polymerized form, but to the complex mixtures of salts.

Of great interest to environmental chemists, ESCA has been shown, at least in preliminary experiments, to be useful in performing such studies as the determination and study of arsenic in soil samples. Spectra of various arsenic compounds were taken along with that of the arsenic containing herbicide, cacodyllic acid, and some forest soil inoculated with the herbicide. Difficulty was encountered in getting reproducible data on the cacodyllic acid and the As_2O_5. There was no difficulty in detecting the arsenic in both the soil samples and a water extract of the soil. Although the binding energies indicated for these samples fall in the broad range found for As_2O_5, more experiments are necessary to conclude that the arsenic for the pesticide is actually in the form of As_2O_5 in the soil.

An important industrial application of ESCA as a quantitative tool involves the determination of relative amounts of MoO_3 in commercially produced MoO_2. Until now, no instrumental method had been developed for such an analysis because of the difficulty in detecting one oxide in the presence of another. Swartz and Hercules[14] conducted experiments on various mixtures of MoO_2 and MoO_3, comparing peak heights as an indication of the relative amounts of each species in a sample. A calibration curve yielded a straight line. Since the focusing current of the spectrometer varies with MoO_2 content, a complete scan of the entire molybdenum 3d electron spectrum was necessary each time.

If the peak separation of two oxides is sufficiently large and the species with the lowest oxidation state is stable to further oxidation, the above technique may be used for quantitative analyses of any two commercial oxides. At least three other pairs have been found to fit the qualifications—PbO–PbO_2, Cr_2O_3–CrO_3 and AsO_3–As_2O_5.

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CONCLUSIONS

The studies reviewed in the present paper have been selected because they are illustrative of areas where important contributions may be made to environmental studies. The ability to define the nature of a material on a surface is important in both air and water pollution studies. For example, ESCA analysis of sediments should be very useful in studying water pollution incidents. Also, they should be very helpful in studying the nature of the chemical reactions occurring on clays.

The ability of ESCA to separate oxidation states of the same element is of potential value. It is well known that the form of a specific pollutant determines its toxicity. For example, organomercury compounds are highly toxic, while bichloride of mercury was formerly used as a laxative. In air pollution studies, ESCA should be valuable in determining the exact form of a particular pollutant. It should be possible to distinguish particulate lead from lead oxides.

Quantitation is important to any analytical procedure. The studies reviewed here indicate that ESCA can be used as a quantitative technique, although much is still to be learned about the experimental factors affecting a quantitative measurement. With improved calibration techniques however, ESCA should become a widely applicative quantitative tool for any material on a surface.

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