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The present review is on the subject of surface analysis and includes the fields of X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) for the period of 1979–1981. This review will cover the literature abstracted in Chemical Abstracts between September 3, 1979, and November 2, 1981 (plus some important articles that have appeared in the latter part of 1981). The reviews of XPS, AES, and SIMS are written as separate sections for the reader’s convenience.

XPS, AES, and SIMS are the most widely used techniques in surface analysis and are often used in combination. Although XPS (and UPS) and AES have been covered by earlier fundamental reviews in Analytical Chemistry (1–5), SIMS is only mentioned briefly in the Application Reviews on Surface Characterization (6). Considering the importance of surface analysis in today’s technology, we thought that XPS, AES, and SIMS should be included in one review.

This review, although lengthy, is not an all-inclusive (2 year) bibliography of XPS, AES, or SIMS. We have tried to select the most important papers in each field that (in our opinion) will advance the “state of the art” of XPS, AES, and SIMS.

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review to a manageable size. Therefore, we apologize if we have overlooked some important paper(s). Researchers have also invited us to reprints of papers that they believe should be included in future fundamental reviews on surface analysis.

The most difficult task in writing this review (other than the task of handling such a large number of papers) is trying to write coherent paragraphs while limiting the scope of the subject to only those papers published during the last 2 years. Therefore, we apologize if the paragraph structure seems "choppy", because it is.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Introduction

X-ray photoelectron spectroscopy, XPS (also referred to as electron spectrometry for chemical analysis, ESCA), has received wide acceptance in the scientific community. The highlight of the reporting period was the winning of part of the Nobel Prize in Physics by K. Siegbahn for his work in photoelectron spectroscopy. A large number of researchers carry out the technique, as can be seen by the many different journals cited in this report. The use of multiple techniques in a given study is increasing, and the combinations are too numerous to list.

Volume 4 of Electron Spectroscopy: Theory and Technical Applications (A4) dealt primarily with XPS. The measurement of binding energies and relative intensities is at the heart of most XPS experiments. From these measurements much information about the surface region and atomic environment is derived. Unfortunately, the reproducibility of such measurements between different laboratories has been shown to be poor. Powell et al. (A9) have conducted a round robin survey using Cu, Ag, and Ni with 38 different instruments manufactured by eight companies. Variations in binding energies of 2 eV and intensity variations of a factor of 10 have been reported; part of these differences were ascribed to poor instrument performance.

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Factors Affecting XPS Analysis

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Hazzell et al. (A10) have prepared a chart of binding energies that would be encountered in normal XPS experiments. Such a chart is easier to use than the usual tabulated listings. Bakke et al. (A17) have listed the binding energies for approximately 800 different compounds. The determination of binding energies by the two X-ray wavelength method (Ag Lα and Al Kα) by Bird and Swift (A12) has led to changes for suggested binding energies of noble metals and Co compared to previous reports. Differences of almost 0.5 eV were found. Core level binding energies for Hf to Bi have been measured by Nyholm et al. (A13); differences with other workers in most cases were small.

Adventitious carbon, i.e., carbon from the background contamination, has often been used as a binding energy calibration. Jaegle et al. (A14) have found the peak position for this line can vary by about 1 eV after ion bombardment, depending on the time after sputtering and the substrate. Extra atomic relaxation of the overlayer was used to explain the observed variations. Lewis and Kelly (A15) have suggested a procedure to measure binding energies of insulators while using a monochromatic X-ray source and an electron flood gun. Their proposed model depends on a current balance that leads to the result that for insulators the surface potential should be determined from electron flood gun data.

Wagner (A16) has investigated the use of a hot filament to reduce the effect of charging when a nonmonochromatic X-ray source is used with insulating samples. He noted that the observed binding energies are a function of the operation of the filament; he found also that mixing an insulator and conducting powders does not reduce charging.

Wagner (A17) has proposed that electron spectrometers should be calibrated via the use of the 2p3/2, Auger, and 3p lines from cleaned Cu. For insulating samples the adventitious C Lα line or the gold decoration method was recommended. The influence of surface charging has been investigated by Chadwick and Karolewski (A18). These workers concluded that materials chosen for standards should have a negligible surface atom core shift relative to the bulk, and for atoms in which this effect is large, the kinetic energy of the transition used should be large so as to minimize the surface effect. Thus, the use of the Cu 2p3/2 line suggested by Wagner is questionable. The use of gold deposition on nonconducting samples has been examined by Uwamino et al. (A19); a gold layer of 8 Å was found to be the optimal value from the point of view of consistent binding energies of the nonconducting substrate (after setting the Au 4f7/2 peak at 83.8 eV) and of the fwhm of the various peaks.

Cross Sections. Another factor that has to be considered in the use of XPS as an analytical technique is the relative cross sections between various transitions. Nefedov and coworkers in a series of articles have investigated several aspects of this area. A Monte Carlo type calculation for several different types of samples was carried out. Scattering has a large effect on the absolute peak intensity and angular distribution of photoelectrons (A20). The mean free paths of the escaping electrons are affected also. Photocurrent measurements have been computed for H to Zn with Au Mo and Ag La X-ray lines (A21). Some comparisons with experiment were given.

Goldberg et al. (A22) have computed cross sections for a number of selected atoms. Comparisons to previous calculated values were good. Castle and West (A23) have measured the relative intensities of 45 elements with a silicon Kα X-ray source. (A description of the building of the Si Kα source was also given.) A comparison to theoretical computations was made, and the results were usually in good agreement. Szajman et al. (A24) have studied the use of Al Kα radiation for Li through Pb. After corrections for a contaminate surface, reasonable agreement with Scofield's cross sections was obtained for 1s, 2p, and 3d levels. The comparisons were not as favorable with other levels. Vulli (A25) has measured the asymmetry factor β (which takes into account angular emission factors of ejected electrons) and made comparisons to theory. The agreement was not very good; clearly more work of this nature is needed.

Application of XPS to Inorganic Materials. A recent review has been carried out by several groups. Benziger and Madix (A26) have studied the observed intensities of adsorbates on a Fe(100) surface up to monolayer coverages as determined by LEED. For those elements studied (C, O, S, R), the agreement between experiment and computation is good. Garbassi et al. (A27) have employed mixed oxides of Te-Ni and Te-Ta. Agreement between previous sensitivity factors and experiment was satisfactory.

Inelastic Mean Free Paths. One approach to the determination of inelastic mean free paths (IMFP's) has been to use thin overlayers. With this approach a wide variety of materials has been investigated. Vasquez and Grunthaner (A28) have developed a method to determine overlayer uniformity (in their case, an oxide layer on Ni). They found that the IMFP can vary for nominally the same material; this was ascribed to strained regions that are structurally different. Szajman et al. (A29) have used CdTe overlayers on Ag and found IMFP's of 13-32 Å for electron kinetic energies of 350-1439 eV.

The matrix effect on IMFP's has been investigated by Hirokawa and Danzai (A30). Ni/Cu and Ti/Zr hydrides of the intermetallic compounds with and without matrices of Fe or Mg hydrides showed a matrix effect of 20% or less. The differences in the energies of the lines analyzed were less than 300 eV.

Organic overlayers continue to offer a wide range of reported IMFP's. Roberts et al. (A31) have determined IMFP's of 29 and 33 Å for electrons of 1196 and 1328 eV with thin films of poly(methylmethacrylate) on SiO2. Only a poor E2g energy dependence was noted. Langmuir-Blodgett films of cadmium selenite, a cadmium salt of a diacetylene polymer, and 8-n.
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butyl-10-anthrylpropionic acid have been used by Clark et al. (A32) to determine the IMFP at 1170 eV. Values for the respective polymers were 45, 57, and 70 A; the packing density of the various films appears to affect the IMFP. Hupfer et al. (A33) have employed polymerized layers of the Cd salt of diacetylene carboxic acid on various substrates to obtain IMFP's. They found a range of values from 83 to 121 A for electron kinetic energies of 788-1480 eV; due to scatter in the data, no energy dependence could be found. From these studies it continues to be apparent that the properties of the organic films used play an important part of the reported IMFP values.

Nonuniform Surfaces. The use of XPS for analysis of nonuniform surfaces, i.e., spherical particles, catalyst, and contamination, has to take into account the nature of the surfaces. Cross and Dewing (A34) have found that the evaluation of depth profiles from nonuniform surfaces, when used with overlayers on spherical particles, could be in error by a factor of 2. Also noted was that changes in the takeoff angle did not alter the overlay to substrate ratio. Ebel (A35) has concluded that at low takeoff angles, measurement difficulties predominate, while at large angles, roughness hinders the determination of the thickness of overlayers. A stacking model for nonporous particles has been tested experimentally for Mo oxides and Al2O3 with surfaces areas of 10-200 m2/g by Defoese (A36). The energy dependence has been studied for oxide and contamination layers on Si by Yamada and Kuroda (A37). A simple angular dependent model could describe their results in terms of uniform layers. Ebel (A38) has developed a method to measure overlay thickness that does not require a knowledge of the takeoff angle of photoemitted electrons. The method depends upon assumptions for the energy dependence of the IMFP, photoelectron cross sections, and the measurement of two different energy levels for the same element. Wagner et al. (A39) have investigated oxygen-containing organic and inorganic compounds by observing both the kinetic energy of the KLL Auger transition and the 0 1s peak from the photoemitted 0 1s photoelectron line. With the use of the modified Auger parameter (i.e., the addition of the Auger transition kinetic energy and the XPS binding energy), the data showed that the various classes of compounds had distinct locations in the chemical state plots. The Bremsstrahlung-induced Auger lines (which are above the X-ray photon energy) have been investigated by Wagner and Taylor (A40) for compounds of Al through Si, Br, Mo, Ta, Au, and Pb. The Auger parameter that was computed showed differences of up to several electronvolts for the various compounds containing the same element. Case and West (A41) have investigated several Si-containing compounds and minerals by the same procedure (these authors used a slightly different definition of the Auger parameter). The positions of Bremsstrahlung-induced Auger transitions and the Auger parameter for red P have been observed by Schall and Brunner (A42) and Brunner and Schall (A43) (with a Cu anode) has been used by Holton et al. (A44) to identify the Al 2p line and a plasmon peak for various thickness of Al on Cu. The intensity ratio of the Al 2p to KLL(1s-2s)D2 line decreased as the film thickness increased; these results agree with theory. Thomas (A44) has used a theoretical procedure to understand the relationship between the Auger parameter and the extranomical relaxation energy. In certain instances the numerical evaluations can be somewhat in error. Note: Other examples of Bremsstrahlung-induced Auger transitions are in the Auger electron spectroscopy section of this review.

Satellite Effects. In addition to the main core lines observed in XPS, satellite lines due to shake processes and plasmons are observed often in many systems. Behstedt (A45) has shown that at low kinetic energies of electrons in XPS, the relaxation effect of valence electrons is small and the observed spectrum depends upon the core hole. The shake-up spectra of the N and O levels is levels in para-substituted nitrobenzenes and nitrobenzene, respectively, and theoretically by Distefano et al. (A46). The shake-up lines increased in intensity (up to 50% in some cases) with electron-releasing ability of the substituent. For N,N-dimethyl-p-nitroaniline both in the gas and solid phases, Freudend and Biegelow (A47) have been able to experimentally and theoretically observed the spectra. They suggest that their results were consistent with a negative shake-up energy concept. Loubriel (A48) analyzed the shake-up intensities and energies of Cr(NO)3 by SCF-Xa-multiple scattering calculations. Good agreement with regard to intensity and energy of the satellite peaks vs. experiment was achieved. Loubriel (A49) has used the same procedure to compute the shake-up intensity and energy for Ni(CO)4. The satellite peak was assigned to a 1s to 2s shake-up transition. The satellite structure of the 2p and 3s levels of Fe(III) halides and MnCl2 has been investigated by Scrocco (A50). It was concluded for the case of the 2p transitions that multielectron excitations were most predominant, while for 3s and 3p levels, multiplet splitting was the major component of the satellite structure. Somewhat similar conclusions have been made for the Ni halide 2p and 3p satellite structure by Scrocco (A51). Tse et al. (A52) have observed the shake-up spectra of the dimethyl compounds of Zn, Cd, and Hg for both the main metal and carbon photoemission line. From SCF-Xa-SW calculations, the energies and intensities of the metal shake-up peaks were in good agreement with experiment; for the C shake-up peaks, the calculations yield reasonable values for the energies, but the intensities were markedly underestimated. Cox (A53) has been able to explain the observed regularities in the 3s-3d and 4s-4f exchange splittings. Also it was predicted that correlation effects should remain proportional to the exchange integrals with changes in spin state and valency.

Data Handling. Proctor and Sherwood (A54) have modified the central point smoothing process that many workers use to smooth XPS data with poor signal-to-noise ratios. The procedure involves the use of an estimation of values at the ends of the spectra which allows a large number of smoothing calculations. Examples with noisy data for O 1 s and Sn 3d spectra were given. The deconvolution of XPS spectra by the maximum entropy method has been described by Vasquez et al. (A55). The procedure can resolve peaks that could not be defined by Fourier transform methods. However, line shape information is lost. Davis et al. (A56) have developed a deconvolution procedure for XPS spectra. The instrument/loss function includes a source function, a background function, and an analyzer function. Examples with GaAs, GeS, and GeS were given.
Radiation Damage. Changes in XPS spectra due to the X-ray source have been observed in a number of cases since the technique has become widespread. The number of such instances appears to be less than with the electron beam normally used with AES. Photon-stimulated desorption usually requires photons of a specific wavelength and therefore is observed rarely when the X-ray source has been examined. Copperthwaite (A67) has reviewed a number of systems where changes in the XPS spectrum with time of X-ray exposure have been reported. In addition, other methods of inducing changes (i.e., electrons, high energy radiation, and heating) that have been examined have been reviewed. The need for the coupling of different techniques in studies of this nature has been noted also. The effect of temperature and X-ray exposure time on the N 1s signal of NaNO3 has been examined by Copperthwaite (A58). It was suggested from the XPS spectra that at least four reduction products of NO3− were present in the surface region. The X-ray-induced decomposition of gold(III) dithiocarbamates has been investigated by van Attekerk and Trooster (A69). They have found that the decomposition rate could be reduced by employing a graphite substrate and lowering the sample temperature. The effect of UV radiation on graphite fluoride in various solvents has been monitored by Watanabe and Ueno (A60). They found that the C-to-F ratio increased and the relative number of CF2 and CF3 groups decreased with increasing exposure. Grünther et al. (A61) have used the electron flood gun source, that often is employed to reduce charging, to investigate changes in the Si/SiO2 interface region. They have observed a decrease in the Si 2p peak with increasing exposure. They also noted the effect of the flood gun potential on the position and fwhm of the Si and O XPS peaks. Damage due to low energy ion bombardment on transition metal sulfides has been studied by Coyle et al. (A62). They observed large differences in beam dosages with increasing formation of the metal and sulfur from Fe to Cu; an inverse relationship with the metal and sulfur from Fe to Cu; an inverse relationship.

Hansson et al. (A53) have studied the transmission function of an hemi-mirror and a half-spherical analyzer. The analyzer can operate at a given point, or entire sample analysis. Richter and Peplinski (A64) have used the electron beam with a collimator to passivate the substrate. Areas of interest can be scanned by XPS. The material to be analyzed is an anode that is bombarded from behind by an electron gun; electrons are ejected toward an energy analyzer. Lateral resolution on the order of 15 μm was achieved.

Analysis of Various Materials

Depth Analysis of Layers. XPS is usually not used for depth profiles or layered materials analysis because most systems are not capable of making continuous determinations during sputtering. This is not a limitation with most AES systems. The use of XPS for measuring depth profiles by knowing the angle of the escaping photoelectron has been proposed independently by Nefedov (A74) and Pijolat and Hollinger (A75). Nefedov has considered several different concentration gradient profiles and has computed the variation in intensity with the escape angle. Typical errors were not greater than 20%. Pijolat and Hollinger have studied the effect of escape angle for three systems, Ag/AlOx, SiOx/Si, and Ni/Cu. From both experimental and computer simulation results, it was suggested that a depth resolution of approximately 10 nm was achieved. More recently, Suoninen et al. (A76) have investigated the energy shifts of Ga photoelectron and Auger lines and P photoelectron lines between an oxide layer and a substrate of GaP. They concluded that differences found for oxidized samples and differences from changes in the Fermi level pinning position of the substrate and not to changes in the substrate structure or extra atomic relaxation charging or an interface dipole.

The effect of ion bombardment on a sample has been examined by Rivière (A60), who used XPS to study tin plate passivated by dichromate. Different profiles with respect to Cr concentration have been observed with the same counting rate as an unprocessed commercial analyzer. Read (A66) patented an analyzer that incorporates both a cylindrical mirror and a half-spherical analyzer. The analyzer can operate in a raster mode for spatial analysis, regional analysis about a given point, or entire sample analysis. Richter and Peplinski (A64) have used the electron beam with a collimator to passivate the substrate. Areas of interest can be scanned by XPS. The material to be analyzed is an anode that is bombarded from behind by an electron gun; electrons are ejected toward an energy analyzer. Lateral resolution on the order of 15 μm was achieved.

Alloys and Solid Solutions. The investigation of alloys by XPS can lead to several useful areas of more practical importance. Comparisons with calculated binding energies can lead to several useful areas of more practical importance. Good comparisons were made with radio-labeled techniques.

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adhesion, etc. However, there are a number of areas where fundamental information is reported. Dilks (A97) has reviewed the use of XPS for the analysis of polymers with a number of applications. Most reports usually are concerned with core level spectra, but work on the X-ray-induced valence spectra of polymers has been summarized by Fireux et al. (A98). Multicomponent block polymer surfaces have been studied by O'Malley and Thomas (A89). The use of intensity ratios, variable takeoff angles, and shake-up satellites in the analysis of these surfaces was illustrated. Dilks (A90) has observed that peroxy linkages in polymers fall into two regions of binding energy, i.e., \( \sim 534 \text{ eV} \) for peroxides and \( \sim 535 \text{ eV} \) for peracids, peresters, oxetanes, dioxiranes, and malozonide. The peroxy features are unstable in the X-ray flux.

The use of chemical reactions to characterize polymers has been employed by several groups. Everhart and Reilly (A91) have derivatized the surface of plasma modified polyethylene. A vertical inhomogeneity for N and O was noted via angular dependent measurements; also, decomposition was found in some cases. These workers also observed the effect of various solvents on treated polymers and noted that some functional groups were mobile on the surface (A92). Copolymers of vinyl chloride and vinyl acetate, with or without vinyl alcohol, have been investigated by Pennings and Bosman (A95) by hydrolytic or thermal reaction with dichloromethane or chloroform. The extent of alcohol and acetate groups on the surface then was monitored by the amount of fluorine observed. Bigelow et al. (A94) have sulfonated polystyrene and found by angular resolution measurements that with more-mobile groups on the surface the thermal instability was decreased. The photooxidation of polystyrene has been studied by Peeling and Clark (A95) who observed that several carbon–oxygen moieties were formed. From the disappearance of the C 1s shake-up peak, it was concluded that the oxidation occurred on the phenyl group.

Andre et al. (A96) have reviewed the attempts to understand the XPS spectra of various polymers (e.g., block or alternating structure) via ab initio calculations. In addition, the calculated bond alternation in linear chains (e.g., polyacetylene) were considered. Nonempirical LCAO-MO-SCF calculations have been made on a number of nitrogen-containing polymers by Clark and Harrison (A97). They found that for certain functional groups a simple additive model was inadequate to explain the experimental results. Examples of the use of XPS for analysis of polymer surfaces will be given in the section on applications.

**XPS of Compounds.** Listed in Table I are reports on the XPS of various compounds. As can be seen, a wide variety of materials has been studied. Parameters such as binding energies, substituent, and structural effects have been reported. The information that is contained in these papers should be of use to those with interest in the listed or similar compounds.

**Applications.**

XPS has been used to study a wide variety of materials in order to obtain practical information about the surface region and electronic structure. The articles cited below are not inclusive as to the uses to which XPS has been placed but do offer an indication of some of the applications that have been reported. These areas are polymers and organic compounds (A98–A101), polymers from plasma reactions (A102–A110), biological and related materials (A111–A119), adhesion (A119–A121), soils (A120), and insulators (A121–A122). Ion selective electrodes (A130–A133), silicon and glass surfaces (A134–A139), catalysis (A140–A158), thin films (A159–A165), atmospheric aerosols (A166–A167), corrosion (A168–A173), electronic materials (A174–A176), and ion implanted materials (A177–A179).

**Theory.**

Theoretical work has been concerned with such topics as the prediction of binding energies, multiplet splittings, shake–shake–shake events, and the density of states of polymers with a number of applications. Beck and Nicaudies (A185) have suggested that a weighted Lowdin orthogonalization procedure with proper factors could be used for construction of basis sets. Shung and Langreth (A181) have found that asymmetry due to the difference between the threshold mid core energy follows a simple power law fairly well. This is in spite of the fact that the Hamiltonian used near the threshold does not appear to be valid at a first approximation.

Broughton and Bagus (A183) have computed the most common core level shifts and related relaxation energies for metallic and semimetallic elements and the anions of the halogens and chalcogens. They have concluded that the effects of core–valence and valence–valence interactions can have an influence on core level shifts. The is photoelectron spectrum of Li has been calculated by Larkins et al. (A183) by Hartree–Fock or configuration interaction procedures. Good agreement with regards to binding energy and shake-off processes was achieved. A unified approach with a nonseparable core–hold conduction-electron scattering potential has been used by Bosman et al. (A184) to correlate the XPS spectra of simple metals and semimetals. Agreement with experimental results for alkali metals and halides was achieved. The prediction of binding energies by a Dirac–Fock program for a number of elements has been made by Key et al. (A186). For light elements, relativistic corrections were found to be significant; in most cases the calculated results were within 1 eV of experiment. Clark et al. (A187) has studied the effects of oxidation state and electronic environments on the XPS lines with a LCAO-MO-SCF procedure. They have found that most of the relaxation energy comes from the 3d-valence component. Feldkamp and Davis (A188) have used a simple model based upon the interaction of the 3d band with the 4s valence band for Ni. Researchers agreement for the shape of the 2p\(_{3/2}\) found. Treglia et al. (A189) have concluded that correlation effects within the 3d band of Ni cannot be quantitatively explained by available theory with regards to satellite structure. Two different types of shake-up processes (relativistic Hartree–Fock and Hartree–Fock–Slater) have been shown by McIlpin and Weightman (A190) to give essentially the same binding energies for Zn, Cd, and Hg. Discrepancies between theory and experiment (usually a few electronvolts) were ascribed to many-electron effects. Exchange effects were also able to include some correlation effects into the van Week equation to explain the 3s–3d and 4s–4f exchange splittings. The use of the splittings in XPS spectra to consider changes of spin state and covalency was discussed also.

Ohno (A192) has employed a many body approach to describe the 4s–4p XPS spectra of Pd to Xe. Much better agreement with experiment was achieved with this method than with a quasi-particle approach. Cox et al. (A193) has measured and computed the 3p 3s–3d exchange and the noble gases from 3d using the rare earth metals. An atomic configuration interaction model was used by Boring et al. (A194) to describe the XPS 5p spectra of several actinides. The atomic model could account for the satellite structure without the need of extraatomic relations for shake-up processes.

Several theoretical investigations of organic compounds have been reported. Ficker (A195) has used LCAO-MO-SCF calculations to compute the binding and relaxation energies for different configuration of ethane and ethylene. Agreement with experiment (where available) was within 1 eV. Nonempirical LCAO-MO-SCF calculations have been made on acetone in various configurations by Clark and Harrison (A196). Reasonable agreement for the binding energies of O and C with different atomic environments was obtained; also considered was the core level of the molecule and the shake-up features of the spectrum. Nokagaki et al. (A197) have characterized the energy difference and relative intensity for the N 1s line in a series of nitro-substituted aromatic compounds from the viewpoint of molecular orbitals. The nature of the shake-up process could be predicted from this approach. Bigelow and Freund (A198) have suggested that the N 1s and O 1s spectra of p-nitroaniline can be understood by intermolecular orbital coupling. Boss et al. (A199) have tried to correlate the N 1s line for Malic acid (A190) with a weighted Lowdin orthogonalization procedure with proper factors could be used for construction of basis sets. Shung and Langreth (A181) have found that asymmetry due to the difference between the threshold mid core energy follows a simple power law fairly well. This is in spite of the fact that the Hamiltonian used near the threshold does not appear to be valid at a first approximation.
Table I. Compounds Studied by XPS

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systems studied: major interest

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**References**

portant in lone-pair stabilization.

Green's function methods have been suggested by Born and
Ohrn (A201) for use to compute binding energies in simple
molecules. For H2O and C2H2, good agreement for the valence
band region energies was obtained; but, much poorer results
for the core energies were found. Agren and Muller (A202)
used two different Frank-Condon conditions to compute the
O spectrum for H2O; both methods yielded reasonable agree-
ment with experimental results. The results were in good
agreement to approximately 3.5 eV for FeO was obtained.

Table 1 (Footnotes Continued)

27, 361. 
in better agreement for the Cs than the I. Relativistic Hartree–Fock calculations to predict the 4f binding energies of several rare earth compounds due to different configuration have been made by Herbst and Wilkins (A226). Agreement with experiment to within 2 eV was achieved.

**AUGER ELECTRON SPECTROSCOPY (AES)**

**Introduction**

Auger electron spectroscopy has advanced on many fronts over the past 2 years. Experimental and theoretical improvements have extended the types of analysis possible with AES. The complications of AES have been reviewed by Holloway (B1), and for surface analysis by Wild (B2).

**Auger Line Shapes**

Elements. The line shapes of Auger spectra of numerous elements have been studied in detail during the reporting period. When a valence electron is involved in the transition studied, information concerning the density of states (DOS) of the valence state and the mechanism of the Auger process can be obtained. Gavriljuk and Lifshits (B3) have analyzed the AES C KVV spectrum and concluded that the bonding of the surface is similar to that of the bulk. Lasser and Fuggle (B4) have studied the KL V spectra of Na, Mg, Al, and Si and concluded that the effect of core holes on the localized orbitals was greater on the energy distribution of states than from one another. Gunnarsson et al. (B5) investigated the effect of plasmon gain peaks in the Auger spectra of Na, Mg, and Al. They concluded that a Lorentzian convolution was inadequate to explain these peaks and that interference effects between different plasmon gain peaks broaden the final gain peak. The Auger spectra of Si continue to receive attention. Brockman and Russel (B6) have investigated the LLVV and L3VV transitions for Si(111). They claimed that they were able to find evidence for surface dangling bond states. Agreement with the DOS for the LLVV spectra, but only with a partial DOS, could account for the LLVV spectra. Morgen and Ongska (B7) could explain the LLVV spectra from their study of Si(111) on the 7x7 superstructure from the DOS. These workers also investigated the effect of the adsorption of O2, H2O, CO, and Ar+ bombardment on the LLVV spectra. Aksela and Vayrynen and co-workers have studied the Auger spectra of a number of different elements in gas and solid state. The high-resolution LSMMs and LSNN transitions were observed for free K were interpreted from optical data (B8). For Mn Vayrynen (B9) has noted large differences in the intensities of various cases. The LSMM transitions of Mn between the metallic and atomic state. Inner shell transitions for noble gases were more atomic like while outer shell transition were bandlike. The LSMM transitions of the super-Coster–Kronig transitions have been shown to be responsible for the low intensity of the LSMM transitions. Also LSMM super-Coster–Kronig transitions were observed by Novotny and Pachucki (B10) and Pawelek and Pawelek (B11) and noted near 1 eV in the LLVV peaks for Si and Ni when the incident electron energy was varied from just above the L3 binding energy. Aksela (B12) has determined the kinetic energy shifts between the atomic and solid-state AES LSMM spectra for Cu to Se. A thermochromic model for the Auger process gave good agreement between the experimental and calculated values. Hilaire et al. (B13) have concluded that the LSNN transitions of Pd are bandlike and that the fine structure of these peaks depends on surface structures. Aksela (B14) et al. studied the LMM transitions of Br2 and Kr. An agreement between calculated (lj coupling for the initial state and intermediate coupling for the final state) and experimental spectra for the L3MM, L3NN, and L3NN transitions was found. Disagreement was noted for the L3NN and L3NN cases. Aksela et al. (B15) and Pessa et al. (B16) have studied the LSNN, LSNN, LSNN spectra of Ag through Te, both in the vapor and solid phase. The relative intensities of the Auger spectrum of Ag, Au, and Pd were observed to be consistent with a general trend for the Au type of metal. The sensitivity for group orbitals is similar to that in simpler compounds. Molecular orbitals on the final line shapes was noted. Aksela et al. (B18) have found differences for the NOO Auger line shapes of Xe adsorbed from single layers to multilayers on Pd(001) and on preadsorbed Kr. Shifts in the main Auger peaks between unoxidized and oxidized Sm and Fr have been reported by Netzer et al. (B19). Also, the spectra were characterized by broad, asymmetric peaks. Matthews et al. (B20) investigated the L3NN, L3NN, and L3NN transitions for Ir through Au and observed that discrepancies between earlier theory and experiment may be due to sensitivity of super-Coster–Kronig and Coster–Kronig transitions to configuration.

**Compounds, Alloys, and Complexes**

The line shapes observed in the Auger transitions of various compounds, alloys, and gas–solid reactions have been studied extensively. Madden (B21) has reviewed the use of AES for obtaining chemical information in a large number of systems. Line shape analysis for the study of molecular surface reaction products has been reviewed by Netzer (B22). Bermudez and Ritz (B23) showed that the core–valence (F center) Auger transition for LiF yielded a bandlike final state. Bacon (B24) observed shifts in the derivative AES spectra of elemental B, Si, and Cr and compounds of these elements. Also noted were changes in the energy minima among the various materials investigated. Numerous carbon compounds have been studied by AES. The AES C KV spectrum of graphite exhibited the best agreement with calculations. Selected compounds (Cs and Rb) have shown a transition not present in pure graphite (B25). However, the selection rules for such transitions proposed by Oelhafen et al. (B26) were challenged by Bader (B27). Rye and co-workers have investigated the line shape of alkali C to C2 through C4 by using the technique (B28). Fingerprint spectra were obtained for the linear C3 to C5 and neopentane C KV spectra. A one-electron theory could explain the spectra for methane and ethane, but discrepancies began to appear for propane. Differences were found also for the various cycloalkanes (B29). Several metal carboxylates gave essentially similar C KV spectra (B30) and were compared to a theoretical analysis which suggested that some π back-bonding was involved in the observed transitions. The Auger spectrum of CH2CN (B31) has indicated that the contribution from each C or H was about equal for the total C KV spectra. Also, the intensity depends on the electron intensity of the orbitals, and the hybridization sensitivity for group orbitals is similar to that in simpler compounds. The C and O KV spectra of CO and CO2 have been determined (B31) and compared to a calculated one-electron theory with regards to intensities and energies. Some disagreements were noted.

The monitoring of the L3VV spectra during the oxidation of Cu (B32) have been reviewed by several groups. Aksela et al. (B32) have proposed the detection of a molecular oxygen state, while Lang et al. (B33) have investigated the onset of silica formation. The possibility of detection of incomplete oxidation was discussed. Wildman et al. (B34) have used differences in the Auger spectra to have sulfur and oxygen on surfaces. Study of the stoichiometry of thin oxide films on Si. Hezel and Lieske (B35) showed differences in the Si LVV spectra between amorphous SiO2, Si3N4, and Si oxinitrides with various O/N ratios. In addition, a correlation of energy levels determined from electron energy loss spectra with the observed transition energy gave good agreement. Taylor (B36) has observed differences in the X-ray excited LVV and KLL spectra of Si and Si3N4; the effects of various preparations and ion sputtering were studied also. The ability to detect surface sensitization of hydrogen on the L3VV spectra of Si in Si3N4 has been reported by Madden (B37). Ho et al. (B38) have found a large difference in the L3VV spectra of Pd-Si compared to Si, while the KLL spectra were very similar. The spectra were analyzed on the basis of a partial density of states. A partial density of states for Si was proposed by Schild et al. (B39) to explain the Si L2,3VV line shape of Pd3Si, and oxygen chemisorption altered the line shape. Energy shifts in the LVV spectra of transition metal siliicates relative with Pd were observed by Wambs et al. (B40). The AR+ induced Auger LVV spectra of Si and several metal silicon alloys have been found to be different by Iwami et al. (B41). They suggested that the observed electrons were from atoms just below the surface. Muria (B42) has investigated the LVV spectra of Au-Si and Au-B-Si thin films for several compounds. For sulfides the spectra were analyzed by a cross transition and the final state. With sulfites the effect of the molecular orbitals on the final line shapes was noted.

**ANALYTICAL CHEMISTRY, VOL. 54, NO. 5, APRIL 1982 • 301 R**
Factors Affecting Auger Analysis

During analysis of AES spectra the possibility of various physical factors influencing the observation must be considered. Especially important is the effect of the electron beam used in the determination of many AES spectra and changes arising from ion beams used for sputtering. These, and other effects considered below, i.e., backscattering and the mean free path of the ejected electron, are of extreme importance when quantification is desired.

Sputter Effects. Morgen and Ryborg (B50) have observed the effect of sputtering on the (111) face of Si by monitoring changes in the L$_2$V spectrum. Structural changes (observed by LEED) were observed at ion doses of approximately $10^{17}$ cm$^{-2}$ the Auger line shape had been altered markedly. Queirolo and Pignatel (B51) have observed a buildup of carbide type C on Sn during Ar ion bombardment. CH$_4$ was the source of the C. Differences in the sputter yield in a Cu-Ni alloy have been noted by Rehn and Widersich (B53); changes in the Auger line shape were observed to alter the relative electron yield. Segregation while sputtering at elevated temperatures for O in Nb has been demonstrated by Hofmann (B54). Thus, it is possible that diffusion effects can alter the apparent depth profile and that measurement of diffusion can be made. Differential AES has been used by Frankel and Siconolfi (B55) in a Sn-Pb solder; the Pb-rich phase was removed at a greater rate than the Sn phase.

Electron Beam Effects. The damage due to the electron beam used for most AES analysis has been reviewed in some detail by Fantano and Madsen (B56). The effects of charging, beam heating, and electron excitation have been discussed in some detail. Roll (B57) has examined theoretically the heating effect of an electron beam upon a thin film over a substrate. Under certain conditions, temperature increases of several hundred degrees are possible; comparisons were made with experiments by Roll et al. (B58) on multilayer Ni-Cu films. Ohuchi et al. (B59) have studied the migration of Na in thin films of soda-silica glass deposited on stainless steel. The migration of Na and the Auger signals with time was found to be strongly dependent upon the electron beam energy and to a lesser extent upon the current density. Ashley and Anderson (B60) have developed a model that describes the energy loss mechanism for conditioning electrons in SiO$_2$. In addition, electron inelastic mean free paths that were computed agreed well with experiment where data were available. The effect of the electron beam on the Auger line shapes of various sulfur species have been noted by Miura (B42) and Turner et al. (B61).

Backscattering. The change in the observed yield of Auger electrons due to backscattered electrons has been studied by several groups. Ichimura et al. (B62) have made Monte Carlo calculations to account for backscattered electrons; good comparisons to experimental results were obtained for Al, Cu, and Ag with a somewhat poorer result for Au. Jablonski (B63, B64) has used a Monte Carlo method to compute backscattering for V through Ge, and several alloys. Difficulties of up to 10% between two definitions of backscattering were found with the large discrepancy in the electron beam energies. Gergely et al. (B65) have studied several materials (with a wide range of atomic number) and found that backscattering increases strongly with Z. LeHerity et al. (B66) have concluded that the effect of backscattering on the observed yield is dependent upon the atomic density to determine atomic sensitivity factors.

The escape depth of electrons in Ge has been investigated by AES by Grant and Monch (B67) and their values were in reasonable agreement with other studies. Nishimori et al. (B68) have studied escape depths for Cr on Ti and Fe substrates with AES and disappearance potential spectroscopy. They have concluded that the electron mean free path depends upon both the electron energy and the material under investigation.

Angular Effects. Angular effects on the Auger electron yield with single crystals have been considered both experimentally and theoretically by several groups (B69–B74).

Secondary Electrons. A correction for the Auger electron yield due to secondary electron emission has been proposed by Sickafus (B75), which involves a two-energized Auger line where data were available. Roll et al. (B76) have studied Ag/Pd alloys and reached similar conclusions. Ichimura et al. (B77) have concluded that the electron mean free path depends upon both the electron energy and the material under investigation.

Instrumental Effects. LeHerity and Langeron (B78) have discussed the effects and influence of various physical parameters upon the determination of Auger spectra in quantitative AES analysis. These authors (B79) have compared calculated and experimental AES spectra of Se and Se compounds, both in the vapor and in the solid state, and the importance of backscattering along with differences in atomic sensitivity factors.

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Quantitative. A wide variety of specific systems have been studied by AES in which procedures are given that could be extended to other materials. Kelemen and Wachs (B84) have observed that half a monolayer of carbon on a Ag single crystal did not change markedly the ratio of 396 to 404 eV peaks of the Ag derivative AES spectra. This problem was solved by subtracting the direct energy distribution curves for a surface with a carbon overlayer from a clean Ag surface. The differences in the S AES line shapes for sulfide and sulfates has been utilized by Turner et al. (B61) to determine the ratio of mixtures of compounds containing these anions. A simple addition of the pure compound line shapes (after corrections, for background and electron beam effects) was found to be sufficient. Moreover, it was found that the interface in Cu$_2$S/Cds solar cells has been analyzed by Matsuk and Rams (B85) by the differences in the S LVV spectra of Cu$_2$S and Cds. Duc et al. (B86) have developed a quantitative determination for the ratio of the depth of an overlayer to the mean free path for a homogeneous overlayer; a homogeneous rutile film was used for verification of the procedure. Tokutaka et al. (B87) have derived a method for the qualitative calibration curve for an Auger signal vs. film thickness for an overgrowth thin film by determining secondary electron coefficients. Thin films of Ag on Au and Be on Cu gave reasonable agreement. From changes in the Cu MVV line shape for a Cu epaxial layer on NaCl, Namba et
al. (B88) have proposed that changes in surface topography and electronic structure could be observed. These workers (B89) have also used the same procedure for Pd layers on Cu. In this case both Cu and Pd MVV line shapes were employed. The M_4VV transitions for Cu and Ni (80–110 eV) have been employed by Goto et al. (B90) to determine alloy compositions with the simplest of the models having good agreement with experiment. Mitchell et al. (B91) have been able to achieve quantitative analysis at ±0.3 atomic % of iron oxides during sputtering. Better results were obtained when only the negative portion of the peak-to-peak signal of the Paterson model (B92) was compared to the peak-to-peak heights for various sputtered Fe-Cr and Fe-Ni-Cr alloys to the bulk chemical composition and have found good agreement between the analysis. The effect of backscattering, escape depth, and atomic density appeared to have varied little between the various samples. An iterative method to correct matrix effects has been developed and tested by Sekine and Mogami (B93) for alloys; reasonable agreement was achieved with comparison to electron beam microprobe analysis (EMPA). Jablonski (B94) has found that this model film for EMPA is equivalent to expressions for AES backscattering. Oxide films on Fe-Cr alloy surfaces have been investigated quantitatively by Ishiguro and Homma (B95); the effects of sputtering have been considered also. Hartsough et al. (B96) have observed line shape differences of the materials under investigation using AES and Rutherford backscattering; these results may be used to provide information about sputtering yields and quantitative AES analysis. Genrreestroom (B97) has developed a simple data matrix technique to calculate profile analysis of AES line shape differences of the materials under investigation. The method was applied to two different thin film systems. The variation of the peak-to-peak height of the derivative spectra vs. the total Auger current has been used by Rawlings et al. (B98) to monitor changes in the chemical state of NO adsorption on W. The sensitivity for detection of chemical changes was compared to XPS results. Several different analytical methods have been used by Buitrago (B99) to study Ni-Fe, Co-W. Good results were obtained with the elemental standards. Low-energy ion implantation with known doses of P into Si has been used for calibration purposes for AES analysis by Thomas (B100). In addition, sputter yield information was obtained.

Scanning Auger Analysis. Spatial resolution on the order of 50 nm has been achieved with scanning Auger microprobe (SAM) equipment. This specialized use of AES has been reviewed by Johnson with emphasis on metallographic applications (B101). Formante (B102) has developed SAM for the examination of the crater edge profile from sputtering Ni-Cr multilayer sandwich films. Large lateral magnification factors (×10³) were obtained under these conditions. Moulder et al. (B103) have demonstrated the capability of studying the elemental compositions with SAM. Careful sample preparation was emphasized by these workers for this application. A model to compute the spatial resolution of an electron beam due to interactions with the material under study has been developed by Duruk (B104); the results agreed with experiment for Ti with a beam diameter of 0.1 μm and a beam energy of 10 and 50 keV. A computer program has been developed by Schaffer (B105) with FORTRAN programs to control a SAM. The use of SAM in practical problems has included stress corrosion cracking and the effect of heat treatment on solute concentration at grain boundaries of 7075 alloy (B106), (B107) and grain boundary features in Fe and Ni alloys (B108). Os/Ru-coated and noncoated anodes (B109) and Au–Ni–Cu thin films used for electronic devices (B110) have been analyzed by SAM.

Gas–Solid Reactions. The review of gas–solid reactions has been treated in the previous review by Larabee and Shaffner (B111). However, several studies of gas–solid reactions have been of interest. Concerning reactions with graphite, for example, Reuter and Wittmack (B112) have found an enhanced oxygen uptake on sputter-cleaned Si surface under electron or argon ion bombardment. A similar enhancement has been observed for C_4H_4O and C_2H_2 on Ag, and has been observed on surfaces exposed to an electron beam by Ebina et al. (B113). Lieske and Hezel (B114) have combined ion energy electron spectroscopy and AES to analyze the various types of Si bonds, i.e., Si=O, Si-O, and Si-C that were observed during the oxidation of Si by O. The authors used changes in Si LVV Auger spectra with oxidation. Lanz et al. (B115) have also employed this Auger transition in their study of Si oxidation. With the reaction of N ions and neutrals on Si, Delord et al. (B116) have observed changes in the Si LVV spectra, but none for the N KLL. This result suggests that the chemical state of the electron density increases as a function of the position of the electron in the one atomic environment. By measuring intensity ratios of various LMM transitions for several transition metal oxides and sulfides, Rao et al. (B117) have been able to take determinations of the elemental composition of the oxide formation state of metal. Thus, in the case of oxidation studies, the O KLL intensities did not have to be considered. Dolle et al. (B118) have suggested that changes in the Cr Auger line shapes observed during the oxidation of Cr could be explained by an interatomic transition with the 2p levels of oxygen.

AES Analysis. AES has been utilized to investigate numerous systems of practical importance. Some examples are given in Table I.

Depth Profile Analysis. AES has found wide use as a method for depth profiling with numerous systems of commercial importance having been investigated. The topography of the surface under investigation has received attention recently. Maki et al. (B119) have made calculations on the artifacts that result with the profiling of nonflat surfaces, e.g., wires, fibers, etc. The production of a lap taper to facilitate depth profiling has been considered by Lea and Seah (B120); in many instances such a procedure can reduce analysis time. Such factors as the material under study and the distance of an interface from the surface were considered. Kempf (B121) has developed an interference technique that is capable of depth resolution of <1 nm. The procedure is based upon measuring the phase difference between two laser beams; one beam is focused on an area that is free of interference and the other on an unpainted portion of the sample. Guglielmacci and Gillet (B122) have developed relationships to understand the concentration gradient effect and to convert sputtering times to depth. Examples were given with tantalum foil, the epitaxial compounds. The Si–SiO_2 interface has been studied by Helms et al. (B123), in which models for escape depth and ion knock-on broadening were developed. Microtopographical features for depth profiles of porous Al anodes have been investigated by Sun et al. (B124). Such factors as reduction of the Auger signal, changes in the depth scale, loss of depth resolution, and changes in surface topography had to be considered. Malherbe and Hofmann (B125) have studied the depth profiles of low energy N implants into Cr and compared the results to a theoretical model. Feibelman (B126) has compared depth profile results of passivated ferritic steels with experiment given by tantalum foil. The latter techniques were able to identify Mo in small amounts, whereas AES could not; the major elements were observed with all of the techniques. Listed in Table III is a limited number of examples of sputter profile studies.

Theory of the Auger Effect

Work has continued in an effort to gain a greater theoretical understanding of the Auger process. Such knowledge will increase the usefulness of Auger spectroscopy in routine analytical situations and also will lead to more information on chemical bonding. However, the problem of interpretation is not simple, since the Auger process is a two-electron process and no easy and clear set of selection rules exists. In addition, multiplet splitting further complicated the evaluation of experimental spectra. The next few years should show even greater understanding of the Auger process.

Yeibelman (B127) has proposed that the rate of reneutralization of the two holes on a single atom is of the order 10⁻¹³ s⁻¹. This "bottleneck" can then account for the desorption of an ion from a surface. Schuman and Dow (B128) have used a mean-field model to compute the Auger line shape for Li. The model is based on the same assumptions as the previous models. This model has been able to account for the line shape in addition to band effects as suggested by Jennison. Jennison et al. (B129) have analyzed the Auger line shape for Be and found that valence band narrowing effects can contribute to the understanding of the line shape for this metal. The analysis of Auger line shapes for several simple hydrocarbons and Cu and Be has been made with some success by a simple one electron theory with uncorrelated final state hole motion by Jennison (B130). However, initial state
relaxation and screening for metals have to be considered for details fits. Hartree–Fock–Slater transition state calculations by Sen (B131) of the Auger KLL transition energies were within a few evolts of experimental for Na and Mg. The breakdown of the one-electron model to describe the M_{n}N_{m}N_{o}KLL Auger transitions for Pd to Te has been considered by Ohno and Wendin (B132). A Coster–Kronig fluctuation was ascribed to the level shifts and broadening observed. Thomas and Weightman (B133) have examined the ratio of the Coulomb repulsion to energy separation for two single particle bonding and antibonding states for simple diatomic molecules. The effect of this ratio on the multiplet structure on small diatomics will be small, but for larger molecules the effect should be larger. Ageren (B134) has used ab initio techniques to describe the molecular valence spectra of several fixed gases. The assignment of the various transitions was aided by the fact that the spectra could be divided into three separate regions; configuration interaction was found to be important in this analysis. Jennison (B135) has concluded that inclusion of initial state core hole projected on the final state reduces the error in peak intensities from up to 70 to an average of 20% in the calculation of the KLL Auger spectra of NH3. Jennison et al. (B136) have concluded that configuration interaction is important to compute the Auger spectra of unsaturated polar molecules while one electron results can agree with experiment for nonpolar unsaturated molecules. Kosugi et al. (B137) have developed a simple empirical approach to describe the Auger spectra of simple gas molecules that is based upon single ionization potentials. However, the testing of the procedure involved transitions in which the two holes of the final state are different. Dunlap et al. (B138) has tested the possibility of using ab initio Xα-type calculations to analyze Auger spectra. Qualitative agreement was obtained for Oα and suggestions for improving agreement between experiment and theory were made. Kulheim and Faegri (B139) have concluded that correlation mixing must be included to adequately describe the experimental spectra of HF; it was not as important for Ne.

Ramaker (B140) has investigated final state correlation effects on the Auger O KLL and Si L_{α}VV spectra in SiO2. The O KLL spectra suggested strong localization around a single SiO2 cluster, while the Si L_{α}VV spectra had both local and nonlocal contributions. Also obtained were good values for an average of 20% in the calculation of the KLL Auger spectra of NH3. Jennison et al. (B136) have concluded that configuration interaction is important to compute the Auger spectra of unsaturated polar molecules while one electron results can agree with experiment for nonpolar unsaturated molecules. Kosugi et al. (B137) have developed a simple empirical approach to describe the Auger spectra of simple gas molecules that is based upon single ionization potentials. However, the testing of the procedure involved transitions in which the two holes of the final state are different. Dunlap et al. (B138) has tested the possibility of using ab initio Xα-type calculations to analyze Auger spectra. Qualitative agreement was obtained for Oα and suggestions for improving agreement between experiment and theory were made. Kulheim and Faegri (B139) have concluded that correlation mixing must be included to adequately describe the experimental spectra of HF; it was not as important for Ne.

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for a series of Cl-containing compounds. Their results obtained from CI KLL and 2p ionization energies agree with experiment and simple theory substituent effects.

Combined XPS-AES Topics

The similarity between and the ability to do both XPS and AES in the many commercial systems has led to a combined approach in which the combination of techniques has enabled investigators to obtain much more information on a particular problem than could be provided by only one of these procedures. Also many of the problems are common to both techniques and the individual sections strongly favored one procedure over the other when multiple procedures were used. Those listed in this section have a more balanced point of view. The topics covered will be roughly the same as those indicated for the individual techniques. The reader should examine those portions of interest (e.g., mean free paths, etc.) in all of the sections in order to have a full picture of the area.

The use of combined techniques has been reviewed by Shemenosi (B145) for quality control purposes, environmental particle analyses by Natuah (B146), surface quantification by Powell (B147), polymer technology by Holm and Shorp (B148), and glass technology by Fox (B149). Chang (B150) has compared the techniques with regards to sensitivity, speed, spatial and depth resolution, chemical bonding information, sample damage, and development of analysis, and in the individual sections strongly favored one procedure over the other when multiple procedures were used. Those listed in this section have a more balanced point of view. The topics covered will be roughly the same as those indicated for the individual techniques. The reader should examine those portions of interest (e.g., mean free paths, etc.) in all of the sections in order to have a full picture of the area.

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as protonated, cationized, and deprotonated molecular-like ions.

Fast atom bombardment (FAB) and other neutral beam sources are also being used in SIMS. The FAB technique, in particular, has made considerable progress in the analysis of biological/macromolecules. Recent developments in FAB are therefore included in this review.

This fundamental review of SIMS (and related techniques) is divided into four sections. The first section reviews the theoretical aspects of sputtering and the mechanisms for secondary ion formation and emission. The second section reviews various instrumental developments. The third section discusses the methods used in quantitative SIMS analysis including depth profiling. The last section deals with the formation and emission of polyatomic and molecular ions in SIMS and includes a discussion on analyzing nonvolatile and thermally labile materials.

Books, Conferences, Reviews. A source book on SIMS is not yet available. SIMS, however, has been the subject of several book chapters, review articles, symposia, international conferences, and workshops during this review period. With this in mind, a source book (C1) discussed “New Developments in Secondary Ion Mass Spectrometry” as part of a symposium on Applied Surface Analysis at the 28th Pittsburgh Conference on Analytical Chemistry in 1978. The paper (published in 1979) includes a discussion of in-depth profiling, depth resolution, high mass resolution, qualitative/quantitative analyses, detection limits, element mapping, nonplanar surfaces, and quadrupole/magnetic mass spectrometers in SIMS.

Two international SIMS conferences (SIMS II and III) were held. SIMS II convened at Stanford University on August 27–31, 1979. The complete proceedings of the conference contain over 80 invited and contributed papers on fundamental aspects (13 papers), quantitation (10 papers), semiconductors (11 papers), static SIMS (8 papers), metallurgy (8 papers), instrumentation (13 papers), geology (6 papers), biology (7 papers), combined techniques (9 papers), and three postdeadline papers (C2). The proceedings present an excellent survey of SIMS.

The Third International SIMS Conference was held in Budapest, Hungary, on 30 August–6 September 1981. The proceedings of this conference are not yet published. Several pointed-workshops were also held during this review period. One workshop (C3, C4) dealt with “Ion Formation from Organic Solids” and compared spectral similarities between SIMS, field desorption, plasma desorption and laser desorption mass spectrometry. The proceedings of this workshop will be published in early 1982 by Springer. The Middle Atlantic Mass Spectrometry Laboratory sponsored two symposia on fast atom and ion-induced mass
spectrometry of nonvolatile organic solids. One of the meetings is discussed in a recent article (C9).

The Annual Conference of the American Society for Mass Spectrometry (ASMS) presents a variety of papers on SIMS, FDMS, LDMS, and PDMS (C6). The 29th Annual Conference held in Minneapolis on 24-29 May 1981 conducted a special FAB symposium in which over 15 FAB papers were presented.

The Fourth International Conference on Ion Beam Analysis was held in Aarhus, Denmark, on June 25-29, 1979. The proceedings of the conference published in early 1980 (C7) contain most of the 126 contributed papers. The major topics are stopping power and straggling (16 papers), cross sections for ion-beam analysis (13 papers), methods and apparatus (23 papers), radiation damage, defects, and diffusion (13 papers), sputtering processes and SIMS (17 papers), applications to arts and archaeology (6 papers), new applications of ion-beam analysis (24 papers), and surface studies (14 papers). Some of the papers pertaining to depth profiling and SIMS will be discussed later in this review.

The Eighth International Mass Spectrometry Conference was held in Oslo, Norway, in August 1979. The proceedings of the conference published in 1980 (C8) fill two 3 in. thick volumes with 290 papers on state-of-the-art mass spectrometry. The volumes contain a short section (10 papers) on SIMS and an excellent section (20 papers) on the ionization of nonvolatile compounds. Most of these papers are discussed individually throughout this review.

A large number of review articles on SIMS appeared in 1979-81. Table V lists the recently published review articles on SIMS and related topics. The articles that are particularly noteworthy include two SIMS bibliographies written by Yin (C37) covering the period 1958-1975 and by Baum (C30), an extensive review article by Conzemius (C50) with 462 references covering the applications (to solids) of the laser ion source in mass spectrometry, and an excellent article by Werner (C32) on "Modern Methods for Thin Film and Surface Analyses" comparing the analytical features of laser optical emission spectroscopy, XPS, AES, electron microprobe analysis, scanning and transmission electron microscopy, low and high energy ion scattering spectroscopy, and SIMS.

Applications. Some recent applications of SIMS and related techniques are listed by category in Table VI. The individual references contain a few key words that describe the subject of each paper.

Sputtering Theory and Mechanism

Atomic and molecular particles are ejected from solid surfaces by the impact of energetic particles. The phenomenon known as sputtering is important in today's science and technology. Sputtering phenomena are fairly well understood for simple elemental targets but become much more complex for multicomponent or molecular systems. An understanding of the basic processes associated with the formation/emission of ions during sputtering is critical to the application of SIMS for the chemical analysis of surfaces. To what extent the ejected secondary ions represent the virgin surface is a primary concern in SIMS.

Constructing a comprehensive theory of the secondary ion emission process based on SIMS results alone will be very difficult without placing into proper perspective the interrelation of bombardment-induced ion, neutral, electron and photon emission. The ion emission process can be treated in two steps: collisional sputtering and particle ionization.

Collisional Sputtering. Most of today's knowledge about the experimental and theoretical aspects of sputtering has recently been collected and summarized. One source consists of the published proceedings of the Second International Workshop on Inelastic Ion-Surface Collisions held at McMaster University (Hamilton, Ontario) on 14-16 August 1978 (C190). The volume contains 28 papers, consisting of review articles on radiation damage (C196), ion-induced electron emission (C197), photon-induced sputtering (C198), thermal effects in sputtering (C199), total current spectroscopy (C200), bombardment-induced light emission (C201), gas-phase collisions (C202), ionization processes in secondary ion emission (C203), energy dependence of the ionization probability (C204), electron and photon desorption mechanisms (C205), sputtered ion emission (C206), and other contributed papers.

The proceedings of the Third International Workshop on Inelastic Ion-Surface Collisions held at Feldkirchen-Westheim, Fed. Rep. of Germany, on September 17-19, 1980, contains 29 papers on the topics of electron emission, electron and photon impact, electron transfer, polarized light emission and excited particle emission during sputtering (C207). The volume contains 14 major review articles on the sputtering process including theoretical aspects of electron emission during ion bombardment (C208), ion-induced Auger electron emission (C209), interaction of metastable atoms with surfaces (C210), angle-resolved electron and photon stimulated desorption (C211), Auger-initiated desorption (C212), electron capture (C213), and electronic excitation and collisions (C215), charge fractions (C216, C217), polarized light emission (C218), outer-shell excitation (C219, C220), theory of charge states (C221), ion and excited state formation (C222), and velocity measurements (C223).
SURFACE ANALYSIS

The Eighth International Conference on Atomic Collisions in Solids was held in Hamilton, Canada, on 13-17 August 1979. The proceedings of the conference (C224) contain 105 papers: 7 papers on coherent radiation, 11 papers on molecular ion break-up, 10 papers on channeling and blocking, 6 papers on ranges, 6 papers on energy loss, 8 papers on projectile and target state changes on high density collision sputtering, 11 papers on radiation damage, 6 papers on trapping, adsorption, and emission, 7 papers on surface scattering, 6 papers on surface charge exchange, and 7 papers on electronic photoemission. These papers will be discussed in detail in the following sections of this review.

The Ninth International Conference on Atomic Collisions in Solids was held in Lyon on July 8-10, 1981. The proceedings are to be published in Nuclear Instruments and Methods.

Springer-Verlag will publish three volumes in their Topics in Applied Physics series on "Sputtering by Particle Bombardment". The first volume (C225) deals with the physical basis for sputtering of single element solids. Chapter 1 by R. Behrisch gives a general overview and introduction to sputtering yields, calculations, and applications. Chapter 2 by P. Sigmund begins with a historical survey of the different sputtering theories and the classification of sputtering events as knock-on sputtering or elastic collisions and electronic excitations. A more comprehensive theoretical model of the sputtering process is based on computer simulations, and that their formation is strongly dependent on crystal orientation of the target and on the site geometry of atomic or molecular adsorbates.

Chapter 3 by M. T. Robinson deals with theoretical aspects of monocrystal sputtering including effects due or caused by the structure of surfaces, radiation damage, and surface binding energies. The ideas of crystal transparency and channeling aid in understanding the effects of orientation and the sputtering yield. A more comprehensive model of the sputtering process is based on computer simulations. Several examples are given that include displacement cascades in stable, metastable and quasistable dynamical modes and with the binary collision approximation. In Chapter 4, H. H. Andersen and H. L. Bay present an overview of all reported results about different methods to determine total and differential sputtering yields and their dependence on ion mass, energy, and angle of incidence and on target structure and temperature. The yields are depicted on a set of graphs and some are compared to Sigmund's sputtering theory. In the fifth and final chapter, H. E. Roosendaal discusses sputtering yields of single crystals and the dependence on crystallographic orientation of the target and on the target-substrate interaction potential. Particular attention is made of the channeling model.

The remaining two volumes are not yet published. The second volume will deal with the sputtering of multicomponent targets such as alloys and compounds, chemical sputtering, and sputtering by electrons and neutrals. The third volume will present information about the angular, energy, mass, and charge-state distribution of sputtered particles.

Other papers dealing with collisional aspects of sputtering include theoretical studies on the depth of origin of sputtered atoms (C226), atomic mixing by ion beams (C227), sputtering from elastic-collision spikes in heavy-ion-bombarded metals (C228), low yield sputtering by backscattered ions (C229), the emission of atoms and electrons from high density collision cascades in metals (C220), threshold studies of secondary electron emission induced by macro-ion impact of solid surfaces (C231), transport theory for kinetic emission of secondary electrons from solids by electron and ion bombardment (C229), the influence of the injection energy of adsorbed layers on various metals (C233), and the influence of ion beams on the adsorption process (C234).

Several researchers have also measured the velocity and energy distributions of sputtered neutral atoms. They showed that the LIF method could be used to obtain velocity distributions of sputtered neutral atoms, and possibly, of sputtered ions and excited atoms and ions. Snowdon and Macdonald (C237) measured the population distribution of the rotational and vibrational states of CH during gas phase collisions and sputtering of an adsorbed hydrocar bon layer. They found that the process leading to the ejection of the electronically excited molecule is governed by a direct projectile-adsorbate interaction but not by the conditions of the thermodynamic or many-body cascade model. (Taglinski et al. (C233) also describe ion-impact desorption as a direct projectile-adsorbate impact phenomenon.) Tsong and Yusuf (C238) measured the velocities of sputtered excited atoms and found that excited atoms are formed early in the sputtering process, i.e., after the first few collisions. Thompson and co-workers (C239) discuss the effect of ion mass and target temperature on the energy distribution of sputtered atoms.

Sputtering Simulation. Other research on sputtering that has received much attention during this review period is the computer simulation of the sputtering process by classical molecular dynamics models (C240, C241). These models are used to predict sputtering yield, energy and angular distributions of ejected particles, and mechanisms for cluster formation. Several important results for the sputtering of pure elemental (single crystal) targets show that cluster species form by recombination in a region above the surface (C242) and that their formation is strongly dependent on crystal orientation of the target and on the site geometry of atomic or molecular adsorbates (C243-C245).

Another result indicates that molecular adsorbates such as CO and H2O are ejected intact from the surface and form clusters with substrate atoms above the surface (C246, C247).

Additionally, the angular distribution of higher energy particles (>20 eV) exhibit strong anisotropies (C248, C249) which can be used to determine the adsorbate positions (C250-C252). Recent theoretical studies of the angular distributions of atomic adsorbates include the effects of bonding site, interaction potential (C254). Harrison (C255) discusses the ion-atom potential function dependence of simulated sputtering and finds that a wide choice of potential functions will reproduce the experimental yields.

Garrison discusses the related theory of ion scattering from single crystals (C256).

One example of computer simulated sputtering from multicomponent systems is the molecular dynamics study of KCl. The study of the angular dependence of the sputtering yield and of the ion-atom interaction potential of KCl (C257) shows that the "sputtered clusters are most likely to represent the undisturbed surface as the primary beam collides at smaller angles." (C257)

Ionization/Ion Emission Models. The molecular dynamics calculations do not currently consider the ionization probability for a given sputtered particle. An alternative more comprehensive ionization theory for sputtered particles does not exist although several ionization models for intrinsic (C203) and chemical (C206) ion emission have been proposed. One promising theory previously developed for ion scattering (C258) explores the probability for ion neutralization near the surface by Auger neutralization, resonant tunneling, and radiative or inelastic transition processes (C259). Murray and Rabalais have also revamped an ionization-neutralization mechanism for molecular ion emission (C260) where resonance and Auger charge-exchange transitions occur between the surface and the outgoing particle.

Winograd and co-workers (C261) have recently added an image force to their classical dynamics calculations for Ni ions. Their calculations show excellent agreement with the experimentally measured angle and energy distribution of Ni+ ions. Two important conclusions of the study are that the ionization probability is nearly isotropic and that it is weakly dependent on particle energy.

The velocity or energy dependence of the ionization probability has also been considered by several other researchers. Lundquist found a simple power dependence on energy for the ionization of Ce and other multielectron ions (C262-C264). Blaise and Nourrier (C203) and independently, Norskov and Lundquist (C265) calculated the ionization probability of secondary ions emitted during sputtering and found an exponential dependence on the normal component.
of the emission velocity. Sroubek, Zdansky, and Zavadić recently argued against such a velocity dependence (C297). Yu found experimentally, however, that the ionization probability $P$ (of sputtered $O^-$ from chemisorbed oxygen layers on V and Nb) was dependent on the normal component of the emission velocity, which suggests that the ionization process is an ion-surface interaction and not an ion-atom binary interaction (C267). Yu used the exponential dependence of $P$ on the sample work function to measure the velocity dependence. The sample work function changes when alkali metals are deposited on the target surface (C267–C270).

In addition to the ionization probability, other atomic properties of the emitted ions such as their stability, energy, etc., must be predictable in order to model their formation and emission, particularly if the ions are polyatomic. Plog and Gerhard recently expanded the "valence model" used to calculate polyatomic ion yields from oxidized metal surfaces and metal oxides (C271). Ganjei et al. correlated negative secondary ion intensities with anion stoichiometry for a series of oxyanions following a modified Poisson distribution model for dissociation of the parent anion (C272, C279).

Several other recent studies address various aspects of the ion formation/emission process. Wittmaack (C274) observed a direct correlation of the ionization probability of $^{26}$Si$^+$ with the Si $L_2,V$ ion-excited Auger electron emission. These results signify the importance of resonance ionization in the ion emission process. The fundamental importance of the Auger process is also observed in the mechanism for electron- and photon-induced desorption (C275, C276). Coles (C277) proposed a surface plasma model in which electron-impact ionization occurs just above the surface producing secondary ion and photon emission; two related papers still question the existence of local thermal equilibrium (C278, C279).

Other studies used the emission of ions, photons, and/or electrons to indicate the intermediate states in a surface reaction (C280), to determine excited state populations and energy distributions of sputtered species (C281–C288), or to compare the absolute yields between excited neutrals and positive ions (C289).

**Instrumentation**

The basic components of a secondary ion mass spectrometer are a primary ion source, a target holder, and a mass spectrometer. The primary ion beam is produced typically from common or inert gases by a conventional ion gun. The ions are extracted from the (differentially pumped) source, focused, and accelerated to energies between 1 and 20 keV before they impact the target. The primary ions sometimes pass through a mass filter to eliminate any fragment or impurity ions that are present (C290). Methods to remove the residual component of the primary ion beam are also used to improve the homogeneity of the ion beam. Rastering the ion beam increases the sampling area needed to increase the sensitivity in static SIMS or to produce flat-bottom craters for depth profiling samples. Once the ion beam hits the secondary ions are ejected with discrete angular and energy distributions. These secondary ions are then collected (by appropriate ion optics), energy-filtered, and mass analyzed. The energy filters commonly used are simple deflection electrodes, parallel plate, electrostatic mirror, cylindrical mirror, and grid retardation/acceleration analyzers. The mass analyzers include quadrupole, magnetic (single and double focusing), and time-of-flight analyzers. As the ions emerge from the mass analyzer, they impinge upon a collector producing secondary electrons. The secondary electrons are multiplied, counted, or measured by pulse-counting or analog devices and stored as a permanent record (on magnetic tape/disk or graph paper). Some instrumentation produces a visual image of the ion (secondary electrons) signal. The processing of the data reflects the needs of the researcher.

**Instrumentation for field desorption (FD), laser desorption (LD)/LAMMA, and plasma desorption (PD) mass spectrometers** differ in the way the secondary ions are produced and detected. In FD, for example, the ions are emitted from a heated tip or needle placed in a high electric field. Recent developments in FD permit ions to be generated at relatively low energies and velocities. Quadrupole mass spectrometers are commonly used (C290). For LD/LAMMA, a continuous wave or pulsed laser irradiates the solid sample to produce the secondary ions (C291). PD mass spectrometry uses a californium–252 radioactive source whose MeV fission fragments desorb secondary ions from the surface of the target as the MeV ions pass through the target (C292). PD experiments usually use a time-of-flight mass spectrometer to analyze the secondary ions.

**Ion Source.** The flux density of the primary ions determines the conditions for "static" or "dynamic" SIMS. The ions in static SIMS are usually stoppable ions (ions in the range of $10^4 \text{ to } 10^5 \text{ A/cm}^2$) whereas in dynamic SIMS they are typically $>1 \times 10^6 \text{ A/cm}^2$. Since these and other ion beam factors such as size, energy, etc., usually require using different types of ion sources, most SIMS instruments are optimized for only one mode of operation. The ion source for the secondary ions can, however, be used in static SIMS even though its current density is $>1 \times 10^4 \text{ A/cm}^2$ (C293, C294). Kloeppe and Seidel have also developed an extremely stable plasma ion source (C295) which produces current densities $>10^6 \mu \text{A/cm}^2$ for ion energies between 0.3–6.0 keV. The plasma source also has a beam profile which is planar.

Bombarding a target with energetic ions causes secondary ions to be emitted. If the target material is nonconductive, its surface can accumulate an electrostatic charge as it neutralizes the incoming ions and emits secondary ions. Several methods have been developed to reduce or neutralize the surface charging. One method bombrates the target with cesium ions (C296) and another floods the target surface with cesium atoms from a cesium evaporator source (C297). Another method makes the cesium on the target surfaces change their electronic properties by reducing the surface work function (while enhancing the yield of negative secondary ions). The cesium evaporator has a similar function to the cesium ion source since it can be used on instruments that already have conventional ion sources (C297).

Another method for analyzing nonconducting targets in SIMS is using neutral beams. One simple design of a neutral beam source uses a conventional metal vapor or chemical ion source (C298). The cesium is neutralized by charge exchange reaction with the metal surface. Another neutral beam ion source neutralizes the ion beam by passing it through a high-pressure gas (C299). If bombarding the target surface with low energy neutrals is also effective in neutralizing the surface charge (C300). A procedure for calibrating an electron flood source has been described (C301).

The purity of the ion beam can have a profound effect on the SIMS experiment and study. Wittmaack and Clegg (C301), for example, extended the dynamic range to $10^6$ for their depth profiling instrument by eliminating the neutral components of their ion beam and by placing the target in ultrahigh vacuum. Methods that remove the neutral component of the primary ion beam are also advantageous (C302). One commercial ion source, the Colutron, uses a Wien-type linear mass filter. The Colutron ion sources have been used recently for depth profiling studies (C302) and to simulate ion impact desorption of impurities from Tokamak walls. The flux density of the primary ions differs in the way the secondary ions are produced and detected. In FD, for example, the ions are emitted from a heated tip or needle placed in a high electric field. Recent developments in FD permit ions to be generated at relatively low energies and velocities. Quadrupole mass spectrometers are commonly used (C290). For LD/LAMMA, a continuous wave or pulsed laser irradiates the solid sample to produce the secondary ions (C291). PD mass spectrometry uses a californium–252 radioactive source whose MeV fission fragments desorb secondary ions from the surface of the target as the MeV ions pass through the target (C292). PD experiments usually use a time-of-flight mass spectrometer to analyze the secondary ions.

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Bombarding a target with energetic ions causes secondary ions to be emitted. If the target material is nonconductive, its surface can accumulate an electrostatic charge as it neutralizes the incoming ions and emits secondary ions. Several methods have been developed to reduce or neutralize the surface charging. One method bombrates the target with cesium ions (C296) and another floods the target surface with cesium atoms from a cesium evaporator source (C297). Another method makes the cesium on the target surfaces change their electronic properties by reducing the surface work function (while enhancing the yield of negative secondary ions). The cesium evaporator has a similar function to the cesium ion source since it can be used on instruments that already have conventional ion sources (C297).

Another method for analyzing nonconducting targets in SIMS is using neutral beams. One simple design of a neutral beam source uses a conventional metal vapor or chemical ion source (C298). The cesium is neutralized by charge exchange reaction with the metal surface. Another neutral beam ion source neutralizes the ion beam by passing it through a high-pressure gas (C299). If bombarding the target surface with low energy neutrals is also effective in neutralizing the surface charge (C300). A procedure for calibrating an electron flood source has been described (C301).

The purity of the ion beam can have a profound effect on the SIMS experiment and study. Wittmaack and Clegg (C301), for example, extended the dynamic range to $10^6$ for their depth profiling instrument by eliminating the neutral components of their ion beam and by placing the target in ultrahigh vacuum. Methods that remove the neutral component of the primary ion beam are also advantageous (C302). One commercial ion source, the Colutron, uses a Wien-type linear mass filter. The Colutron ion sources have been used recently for depth profiling studies (C302) and to simulate ion impact desorption of impurities from Tokamak walls.
instrument. The instrument incorporates a quadrupole mass filter mounted on a flange which can be rotated under UHV conditions in such a way as to vary the polar collection angle of secondary ions; rotating the sample crystal about an axis parallel to the primary ion beam varies the azimuthal angle.

Energy filters are usually used with quadrupole mass analyzers for high-energy ions, single species, peaks etc. The 3M Co. recently patented a new filter-ionizer apparatus for SIMS use (C314). Energy filtering techniques are also used to suppress the intensities of molecular ions (in favor of atomic ions) in order to overcome mass spectral interferences (C315). Energy discrimination effects in SIMS are, however, noted and troublesome (C316).

In depth profiling the target sputter rate is usually determined by measuring the depth of the crater with a Talysurf or interference light microscope. A new electrooptical technique is used for on-line measuring of the sputtered depth during SIMS and Auger electron spectroscopy (C317).

Instrumentation for ultra high sensitivity SIMS has been proposed where single atom detection is possible using dc accelerators (C318).

**Mass Analyzer.** The mass analyzers used in SIMS instruments include quadrupole, magnetic (single and double focusing), and time-of-flight (TOF) analyzers. The quadrupole mass analyzer has several disadvantages over the other analyzers because of its relatively low cost, its compactness, its rapid mass-scan rate, and its ability to operate at or near ground potential. In SIMS, the QMF has been marketed as an "add-on" capability to complement other surfaces characterization such as XPS and AES. Several combination UHV systems have been described (C319-322). In addition, recent developments in QMF theory and design give a better understanding of ion transmission properties (C323) and of ways to collect ions from a large range of initial displacements and/or angles of emission (C326).

The quadrupole mass filters have, however, several problems; the most important ones being severe energy and mass discrimination effects. The magnetic analyzers (and particularly the double-focusing instruments), on the other hand, do not have these problems and in addition, they have better ion transmission and mass resolution and a greater mass range. Recent use of magnetic analyzers in SIMS experiments has produced some astonishing results. Spectral mass resolution of 5000 was achieved by adapting a secondary ion source to a Varian 311A double-focusing mass spectrometer (C325).

Several CEC-110 double-focusing (Mattauch-Herzog) mass spectrometers were configured to high-performance SIMS (C326) and mass-analyzed ion kinetic energy (MIKE) (C327, C328). The high-performance SIMS has demonstrated a mass range of 18,000 amu (C329). Other related (but non-SIMS) instrumental developments include the design of a double-focusing, static, axisymmetric mass spectrometer (C330) and of a high-performance instrument with mass resolution of 10,000-40,000 (C331). Several new scanning techniques for double-focusing mass spectrometers have also been developed (C332) and include a microprocessor control for linked scans (C333), a novel mass marker for metastable ion scans (C334), and a rapid scanning magnet power supply (C335).

Time-of-flight (TOF) mass analyzers have also recently been used in SIMS (C336) and PD (C337, C338) experiments. Klots describes his TOF mass spectrometer as a "poor man's SIMS device" (C339). Templeton and Woodworth describe TOF analyzers with a CMA for simultaneous energy and mass determination of desorbed ions (C340).

The earlier ion microprobes or ion microscopes were designed from magnetic sector instruments. Recent design advances in dynamic SIMS instrumentation (C341) include an ion microprobe mass analyzer of the Liebel-type (C342), a dissector ion microscope mass analyzer (C343), a direct-imaging scanning ion microscope (C344), and a quadrupole-based scanning ion microscope (C345). Levi-Setti and Fox (C346) give a detailed discussion of modern day high-resolution scanning ion probes. They examine the prospects for obtaining high resolution (<150 A) with low-energy ion probes using "effective" imaging microscopes for "destructive" scanning transmission ion microscopy (STIM).

Various data acquisition processing systems for ion microscopes/microprobes have been described (C347-349). A computer program for peak identification of elemental, molecular, and cluster ions in SIMS is also available (C350).

**Quantitative Analysis**

Since secondary ion yields for the elements vary over several orders of magnitude and change with matrix composition and since sputtering and instrumental artifacts also affect elemental sensitivity, quantitative analysis is necessary to determine the true atomic concentrations of the sample. Progress has been made, however, in developing methods for quantitative analysis that convert the measured secondary ion intensities to atomic concentrations. These methods for quantitative SIMS have been discussed recently by Wittmaack (C351), Cappel and Leibfried (C352). The methods that we will review here use enhanced secondary ion yields, calibration curves and sensitivity factors, and glass, metal and ion-implanted standards to determine the true atomic concentrations of the sample. These methods are also applied to the quantitative analysis of depth profiles.

**Sputtering Yields/Ion Yields.** Sputtering yields in single-component systems are readily predicted and measured and are known to depend on the angle, energy, and mass of the primary ion beam and on the structure, orientation, and temperature of the target. Sputtering yields, nevertheless, do not usually vary by more than a factor of 10 for any element. Yield data for the pure elements were obtained recently using 500-1000 eV Ar+ ions (C353). The data compare favorably with predicted values from Sigmund's theory.

A second study obtained sputtering yields for pure metals using 20-keV O2+ ions (C354). Since bombarding with O2+ ions causes oxygen to be implanted into the sample, sputtering yield varies with the oxygen content. Klots et al. (C355) derived the relation for the steady-state sputtering yield and the implanted oxygen surface concentration for different angles of incidence.

Other sputtering experiments include sputtering rates of minerals (C356), sputtering studies in Ar and O2 glow discharges (C357, C358) and sputtering yield measurements of SiC by a volumetric method as a function of target temperature (C359). In the latter study, the yield dependence on temperature is attributed to different sputtering processes.

The secondary ion yields for pure elements vary over several orders of magnitude due mainly to differences in the atomic properties of the elements. While early studies correlated the positive and negative ion yields with the element's ionization potential and electron affinity, later studies showed ion yield enhancements which depend on the composition of the sample (or "matrix effect") and the sampling conditions of the experiment (C353). The presence of oxygen or cesium on the sample surface, for example, enhances the positive or negative ion yields respectively.

In several recent studies, the yield enhancements are correlated with the sputtering yield of the matrix (C360), with the partial pressure of reactive gases like O2 around the sample (C361-363), with the incident ion species such as H, N, O, Cs, etc. (C364, C365), and with the use of reactive ion beams like O+ and Cs+ (C367, C368). In particular, Katz et al. (C360) found a linear correlation between sample sputtering yield and average sample mass. With this relationship the authors could predict ion yields and detection limits of related compounds. In another study, Deline (C367) found the near-surface concentration of the ion yield-enhancing species to be inversely proportional to the sample sputtering yield. However, whether a "unified explanation for secondary ion yields" exists or not remains debatable (C369-372).

Rudat and Morrison (C369, C364) studied the effects of oxygen and nitrogen adsorption on secondary ion energy spectra obtained with reactive ion beams. They conclude that although the energy spectra resemble those obtained from the sputtering of pure elements, a better correlation between different matrices is possible when sputtering in the presence of a high partial pressure of O2 (C364). They also observe abrupt changes in the energy spectra for Ni, Co, and W at high O coverage, apparently due to the incorporation of O into the surface lattice (C364).

Still other "matrix effect" studies try to decouple the sputtering and ionization processes by comparing changes in the ion versus neutral yields. Oechsner and co-workers (C373-375) measured the changes in the ion yields (or ionization efficiencies) as a function of surface oxygen concentration by comparing ion vs. neutral yields.
For the analysis of multicomponent systems, Yu and Reuter caution that one component of a binary alloy bombarded with an O²⁻ ion beam (or an Ar⁺ ion beam with adsorbed O₂) may be preferentially enhanced while the other component is suppressed (C368, C376-C379). Likewise, Modler and Beske (C361) found linear relationships between the secondary ion intensity and element concentration for CuNi alloys bombarded by O²⁻ ions. In another study, CuNi alloys bombarded with Ar⁺ ions give ion yield ratios (Cu⁺/Ni⁺) that are unchanged from that of the pure metals (C361).

A model originally developed for sputtering has been applied to the sputtering of binary alloys and compounds (C382). Betz in an excellent article on alloy sputtering (C383) found preferential sputtering for alloys of intermetallic compounds to be the rule.

Slojdian and co-workers (C384) studied the films formed on Fe, Ni, and Cr under ion bombardment in the presence of oxygen. They showed that the surface of each sample is covered with an oxide film whose composition is the same as that developed on Fe₂O₃, NiO, and Cr₂O₃, respectively, when sputtered under the same experimental conditions.

**Empirical Methods/Physical Models.** Several methods are used to convert measured secondary ion intensities to atomic concentrations. These methods can be grouped into two major categories: methods using various physical properties (i.e., ionization potential, binding energy, etc.) of the sample, physical models, and methods using calibration samples, empirical methods. Although many of the physical models such as the kinetic model, the autoionization model, the surface effects models, and the thermodynamic models (C352) were developed earlier (and continue to be applied), the empirical methods consistently give the best results. The empirical models use calibration standards which are typically made from glass or iron alloys that are chemically and isotopically matched with elements of known concentration. NBS supplies a number of these characterized standards. In quantitative SIMS, relative sensitivity factors for given elements in the sample are determined by comparing the secondary ion intensities for given elements and standards with their respective atomic concentrations. The elemental sensitivity factors can then be used to determine the unknown concentrations of given elements in samples that have the same type of matrix. Two recent experiments using sensitivity factors to study borosilicate glasses have been discussed (C383, C386). Sensitivity factors and practical ion yields are given for Mg, Si, Mn, Fe, and Cu impurities in Al (C387).

The relative sensitivity factor for a given element can also vary with the surface preparation of the sample, primarily if the surfaces are exposed to or bombarded with oxygen (C351, C352). Therefore, a new method was introduced recently which uses changes in the matrix ion species as an internal indicator for indexing the matrix surface properties (C352, C353, C361). This method is known as the MIRF or matrix ion species ratio method. Using the indexed relative sensitivity factors has greatly improved the precision of the analysis (C352). Scilla et al. (C391) recently used the MIRF method to correct for matrix effects in the SIMS analysis of high arsenic (5-5%)/selenium alloys.

Using calibration standards poses several problems in quantitative SIMS. One problem associated particularly with iron alloys or steel standards is the homogeneity of the standard. A recent SIMS study concluded that the NBS steel standards 461-468 and 662-664 are unsuitable as standards in SIMS because all of the elements are not homogeneous within the sampling area of 100 A (C392, C393). Therefore, researchers must be careful in both their choice of standard and what elements in each standard are suitable calibrants.

One way to overcome the sample homogeneity problem has been to develop standards by ion implantation (C394-C399). Here, the concentration and distribution of the dopants can be controlled more accurately, thereby forming standards with better homogeneity. The results with semiconductors, however, have been much more reliable than with ion-implanted metal standards (C397).

In a separate study (C390), McMorran et al. (C397) have described a new empirical method for quantitative SIMS analysis. They use the method of solid-state addition in which they implant their samples with a known concentration of the element of interest. Since the depth profile of the implanted species has a characteristic Gaussian shape, it is easily distinguished from the element originally present in the sample. Therefore, the known concentration of the implanted element is used as an internal standard to determine the concentration of the unknown. Bertrand et al. (C400) have used the standard addition method to detect Pb in lubricating oils.

Another problem in quantitative SIMS is caused by variations of the instrumental factors i.e., to evaluate these instrumental factors, Newbury (C401, C402) conducted comparative SIMS studies of selected glasses and steels with laboratories in the U.S., Japan, and Europe. He had each laboratory calculate relative sensitivity factors for several elements under a variety of experimental conditions. The results were astonishing and showed that a given relative sensitivity factor varied from 5 to 60. He also compared the measured concentrations with predicted values from physical models (C401, C403).

As mentioned earlier, physical models such as the kinetic model, the autoionization model, the surface effects models, and the thermodynamic models (C352) are also used in quantitative SIMS analysis. One thermodynamic model, the local thermal equilibrium (LTE) model, has become very controversial because the values for the temperature and electron density of the assumed plasma (used to solve the Saha-Eggert equation) are unrealistic and nonphysical. The model nevertheless continues to be used in SIMS and for some cases the analysis can be quite good. It is recommended, however, that the model be tested against suitable calibration standards prior to analyzing unknowns (C392, C401-C403).

Other researchers have modified the LTE model producing simplified versions (C382, C394). Morgan (C403, C408) recently described a versatile one-fitting-parameter LTE model with accuracies between factors of 2 and 4. The method is general and not restricted to certain elements in a certain matrix. Several researchers have applied this model to the study of doped GaAs (C407, C408).

The newest thermodynamic model, the local thermal nonequilibrium (LTNE) model, was applied recently to study both pure surfaces and those covered by oxides and other reactive layers (C409).

**Depth Profiling/Microanalysis.** As the sputtering process in SIMS removes successive atomic layers from the solid, the in-depth composition and distribution of elements can be determined by first recording the secondary ion intensity for each element as a function of sputtering time, thus producing a sputtering profile. Only after the ion intensities are converted to their respective atomic concentrations by the quantitative algorithms discussed above and after the time axis is converted to a depth (distance) scale, does the plot become the true depth profile.

The principles of quantitative depth profiling are given in the excellent review by Hofmann (C410). His review is divided into three parts. The first part covers the calibration of the depth scale and ion beam flux. The second part summarizes the problems associated with changes in the surface composition and topography due to sputtering, as well as their influence on depth resolution. The last part summarizes the basic requirements for optimum depth profiling in SIMS.

In depth profiling, the depth resolution of the sputtering experiment determines the quality of the profile. Hofmann (C410) identifies seven factors that contribute to the depth resolution, and other researchers have explored in detail ways to minimize their effects (C411). The first factor deals with instrumental effects that require keeping the primary ion beam pressure of reactive gases below 10⁻⁶ torr (C412, C413) and maintaining the homogeneity of the primary ion beam. The primary ion beam should, for example, be uniform, have a constant ion flux (C414), and be remotely controlled to avoid variations across the sample. The second factor deals with the homogeneity in order to have well-formed craters. Tsong et al. (C415) recently developed an approach to correct for crater effects by examining the number of ions required to sputter a given area with low energy (1 keV) ions (C416), preferably reactive (C351, C417), and the nature of the impurities including carbon (C413). Finally, the ion beam should have a glancing angle of incidence. Even though all of these beam conditions are met, the ions can form on the target surface during sputtering (C418, C419) and are dependent on the angle of incidence of the ion beam (C420, C421). These shapes can be suppressed, however, by using two ion guns incident at different angles (C422).
The second factor deals with initial surface roughness. A recent study found that substrate roughness contributes to the loss in depth resolution due to the orientation of the microplanes making up the rough surface (C423). In another study, researchers found increased surface roughening of Cu bombarded by reactive or noble ions due to "lattice-orientation-dependent sputtering" (C420) and to reorientation effects (C424).

The third factor called statistical surface erosion deals with the original sequential layer sputtering (SLS) model used to predict preferential sputtering and aging associated with the statistical nature of sputtering. The most recent study incorporates site-dependent sputtering rates into the original SLS model, changing the depth resolution from a square root dependence to one that is completely of the order of magnitude away from the original SLS theory. Thus, the statistical sputtering effects are now considered to be minor when compared with atomic transport or instrumental effects (C425, C426).

The fourth factor deals with crystal orientation and imperfections and are largely associated with dependencies of the sputter yields.

The fifth factor on information depth is pertinent for higher energy primary ions only. For these ions, the mean escape depth of the sputtered particles increases with energy (E). The sixth factor deals with preferential sputtering (C383) recently reviewed the sputtering phenomena for alloys and compounds. Although preferential sputtering does not usually occur in dynamic SIMS (for steady-state reasons), the steady-state surface sputtering layer sometimes takes longer to form (C427). Preferential sputtering raises the question of the location of the expected single element diffusion (C421), particularly if a low-sputter-rate impurity is present on the surface. As a special case of preferential sputtering, ion-induced chemical reactions occur when sputtering compounds (C429-C431) or when sputtering with reactive ions (C417).

The seventh factor deals with knock-on and cascade (or atomic) mixing caused by the primary ion beam. A number of theoretical (including model calculations) (C227, C415, C422-C424, C437-C442) studies including an isotope effect study (C443) have been reported. One conclusion of the work is the influence of knock-on and cascade mixing is reduced by using heavy ions at low energy (<1 keV) and at glancing incidence.

The eighth and final factor deals with atomic transport effects such as bulk and surface diffusion, segregation (C444), etc., which can be induced by bombardment or radiation damage. Hofmann (C410) points out that although atomic transport effects are temperature dependent, it is surprising that little information is known about the temperature dependence of depth profiling (C426, C444-C446). As an answer to this question, Rabalais and co-workers (C447) studied the temperature dependence of the positive secondary ion yields from Fe, Co, Ni, Cu, and CuNi alloys. They observed a decrease in temperature dependencies which are caused by the migration of minor amounts of sample impurities. Myc (C448), in another paper, discusses the mechanisms by which ion bombardment influences atomic transport as viewed by cascade mixing, by enhanced diffusion via mobile point defects, by rapid diffusion along extended defects, and by defect trapping. Among the four processes, Myers indicates that defect trapping of interstitials proved most important for high-energy ion beam analysis.

From these considerations, Hofmann (C410) lists the basic requirements to obtain optimum sputtering depth profiles: (1) The ambient environment needs a low residual reactive gas pressure. (2) The sample should be flat and preferably polished. It should also be amorphous and composed of materials of similar sputtering yield. Suitable electrical and heat conductivities are also important so that the sample does not change or decompose when bombarded with ions. (Reuter, et al. (C449) observed unusual charging from targets containing low-conductivity regions.) (3) The primary ion beams should be constant and have a uniform current density. Ion-induced artifacts are reduced when the ion beam is low in energy (<1 keV), reactive, and rastered and has a glancing angle of incidence. Many of these depth profiling principles are exemplified by several extraordinary depth profiling studies of implanted hydrogen (C450-C455), deuterium (C450, C451), carbon (C466), nitrogen (C412), oxygen (C412, C456-C458), and phosphorus (C459). These elements are among the most difficult elements to detect, particularly at trace levels of 10^3 atoms/cm^2. Magee and co-workers have successfully profiled H and D in various Si samples with a sensitivity of <5 x 10^5 atoms/cm^2 and a depth resolution of <100 A, but only after the partial pressure of H_2O was below 1 x 10^-13 torr (C450, C451). Similar conditions are needed to detect P and B in the low 10^8 atom/cm^3 range (C469). Wach and Wittmaack detected <10^9 atoms/cm^2 of N in Si (C412).

Other depth profiling studies detected B in Si in the range of 10^16-10^20 atoms/cm^2 (C469). Cogg (C462) measured the detection limits for important impurities in GaAs ranging from 10^4 atoms/cm^2 for Cr and Mn to 10^24 atoms/cm^2 for Si, Zn, and Sn. Several researchers studied the effects of the use of noble gases in sputtering a variety of ion-implanted species in Si (C463, C464). Leta et al. (C399) measured the projected ranges for 114 individual species/substrate combinations of ion-implanted materials. Slusser and Shuttery (C465) gave some helpful hints for profiling layered structures. And Silber and co-workers (C466) using a scanning ion beam microscope and ion imaging. Schilling (C469) used image-processing techniques to convert the sputtered ion intensities into atomic concentrations. Ruedenauer and co-workers (C471) have developed computer algorithms to remove artifact contrast effects such as topographic, chromatic, or matrix contrast from secondary ion images. Several groups have used modified micrographs or physical techniques for quantitative procedures. Furman and Morrison (C472) used both the modified LTM method and the LTM sensitive mode to quantify their ion images. They also employed ion-implanted internal standards and "imaging standards" to evaluate their quantitative procedures. Furman and Morrison (C473) have developed a multidimensional imaging capability known as MIDAS or a microprobe image acquisition system. MIDAS consists of an ion microscope, a low light level TV camera, a video color graphics system, and computer algorithms for digital image processing and allows for the rapid multidimensional image acquisition and digitization. These developments now permit secondary ion mass spectrometric-image-depth profiling (SIMS-IDP) studies for three-dimensional elemental analysis (C474).

**Polystyrene and Molecular Ions**

Polystyrene or molecular ions predominate the secondary ion emission pattern of most substances whether the substance is metallic, organic, or inorganic. Many researchers, who do quantitative SIMS or depth profiling studies, find polyatomic ions a nuisance because they overlap important spectral regions where atomic ions occur (C315). These researchers have developed, in fact, ways to eliminate (or filter-out) the polyatomic ions. Other researchers, however, use the polyatomic or molecular ions to construct a detailed chemical analysis of the surface (C475-C479).

The formation mechanism of molecular or other polystyrene ions or cluster species by ion bombardment can be broadly viewed either as direct emission of species originating at the surface or the recombination of sputtered species to form new
structures. The direct emission model includes processes such as ejection through momentum transfer in collision cascades, thermal spikes, thermal evaporation, and even agglomeration in a selvedge region or any other unresolvable process that ejects species from contiguous sites. The recombination model, on the other hand, includes processes like ion-molecule nucleation, or association reactions which form species containing constituents from nonadjacent sites. Experimental evidence for the direct emission or the recombination mechanism is ambiguous except for some clear-cut cases for organic and alkali metal cluster ions. For example, Fuerstenau recently described the characteristic features for the emission of cluster ions from thin foils of metals and semiconductors when irradiated with high-energy pulses of UV laser.

Although much theoretical and experimental information is available about the emission of elemental or atomic ions $M^+$, little is known about the formation of the dimer, trimer, etc. Harrison, Garrison, Winograd, and co-workers, however, have recently reported classical molecular dynamics calculations to model the sputtering process for elemental solids (simple crystals) and simple atomic or molecular adsorbates (C240–C242). A principal conclusion of their model is that cluster species do not leave the surface of the solid as intact species but form in a region above the surface by a recombination mechanism. They also conclude, in fact, that the relative inter- and intramolecular bond strength of the solid may dictate the nature of the emission process where species that have strong covalent or ionic bonds may undergo direct emission and those that have weak metallic or van der Waals bonds may undergo recombination (C475).

Cluster ions. One way to elucidate the sputtering and the secondary ion emission processes in SIMS is to understand the formation and emission of cluster ions. An elemental solid $M$, for instance, generally emits cluster ions $M_{n}^+$ whose intensity decreases as $n$ increases. Other experimental features associated with cluster ion emission are reviewed by Blaise and Naumov (C475). Fuerstenau recently described the characteristic features for the emission of cluster ions from thin foils of metals and semiconductors when irradiated with high-energy pulses of UV laser.

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For the sputtering of multicomponent systems such as oxides and alkali metals, as well as the sputtering of elemental targets, Wittmaack and Snowden (C484) discuss the characteristic changes that occur in the secondary ion spectrum of metals during oxygen adsorption and during oxidation. Atomic and cluster ion emission from silicon, silicon oxide, and dopants in silicon have been recently discussed (C485). Wittmaack also presents some generalized rules for the emission of cluster ions from metal oxides (C476). Flog and Gerhard (C486) discuss the physical aspects of the parameters used in the "valence model" to determine the ion yields from oxidized metal surfaces and metal oxides. Wittmaack (C476) gives a different approach to the model. Cluster ions are also formed by sputtering rare-gas solids (C487) and molecular solids (C489–C490). Michl and co-workers studied the SIMS of neat solid Ar, Kr, and Xe as a function of the type and energy of the primary ion, He$^+$–Xe$^+$ (C487). The relative abundance of higher cluster ions increases with the primary ion momentum.

In the case of organic hydrocarbons such as methane (C488), pentane (C489), cyclohexane (C490), and benzene (C490), cluster ions appeared to form by ion–molecule reactions (C475) with no discrete repeating unit. If the frozen organic molecule, on the other hand, have a such as aceton (C489) or are hydrogen-bonded such as formic acid (C491), then the cluster series consists of $[\text{H}(\text{Me})_{n}]^+$ ions. A similar situation is observed for ice where a long series of $[\text{H}_{2}\text{O}_{n}]^+$ ions occurs for $n = 1$ to 50 (C490).

Several other solids composed of small molecules give cluster ions of regular composition, i.e., $[\text{NH}_{3}]^+$ and $[\text{N}_{2}^+]^+$ from solid nitrogen (C488-C489), [CO], and [CO,$^+$] from solid CO (C492), [NO($\text{NO}_{2}$)$_{2}$], and [NO($\text{NO}_{2}$)$_{2}$]+ from solid NO, N$_{2}$O, N$_{2}$O$_{3}$, and N$_{2}$O$_{4}$ (C490), and [O$_{3}$]+ from solid O$_{3}$ (C494). Although the high degree of cluster formation complicates the analytical application of SIMS, Michl and co-workers are able to simplify the mass spectra by diluting the neat matrix with rare gases or by reducing the momentum of the primary ions.

Cluster ions of alkali halides, MX, show intense ions of the type $M^+$, $M^+$, $[\text{MX}]^+$, $[\text{MMX}]^+$, $X^+$, and $[X(MM)]^+$ (C475, C482, C494–C496). Researchers at the Naval Research Laboratory (NRL) recently observed positive cluster ions from C41 extending to the [Cs$_{2}$+$^+$] ion at $m/z$ 18 320 (C496). These high-mass cluster ions are the largest mass-resolved ions ever produced and detected using a conventional mass analyzer (C496, C497) and more than 20 times larger than ions reported by other SIMS instruments.

Although the original alkali halide cluster ion data were interpreted by a recombination mechanism (C482), the NRL group interpreted their data by a direct emission mechanism of sputtering. Their conclusion is based on several results: (1) the most stable ion configuration is that of a bulk "cubiclike" structure, and (2) from a two-dimensional molecular dynamics study of metal halides (C257), cluster ions are more likely to represent the unarranged surface as the primary ion beam impinges at smaller angles relative to the surface.

The structure of the ionic clusters have also been studied by various bond-breaking (C496) and thermodynamic (C498) models.

The formation of cluster ions of alkali halides in field desorption studies are attributed to the effect of a field- and temperature-dependent charging of salt layers by alkali ions (C499). The melting point of the solid influences the ion formation mechanism.

Inorganic Salts. The secondary ion emission patterns from other alkali metal salts such as the alkali sulfates, nitrates, perchlorates, etc., which contain covalently bonded oxinyl ions within an ion lattice, appear differently from the clustering patterns found for the alkali halides (C475). Ganjei et al. (C267, C269) correlated the negative secondary ion intensities with the stoichiometry of the anion. For example, the negative ion pattern (O$^-$, S$^-$, [SO$_{2}$]$^-$, [SO$_{3}$]$^-$, and [SO$_{4}$]$^-$) can be represented by a modified- Poisson distribution if dissociation of [SO$_{4}$]$^-$ and [SO$_{3}$]$^-$ is assumed for sulfate and sulfite, respectively. A recombination mechanism model did not fit the observed intensity distribution (C298).

Other researchers studying similar inorganic systems found that the fragmentation of a given oxyanion is dependent on the nature of the cation, i.e., AgNO$_{3}$ vs. Na$_{2}$NO$_{3}$ (C500) and then the formation of species such as $[\text{MNO}_{2}]^+$ could be explained by a gas-phase statistical recombination mechanism (C501, C502).

Nonvolatile and Thermally Labile Molecules. The recent development of several new ionization methods in mass spectrometry has significantly improved the analysis capability for nonvolatile and thermally labile molecules (C57). Several of these methods, namely, in-beam techniques, field desorption (FD), laser desorption (LD or LAMMA), fast-atom bombardment (FAB), and SIMS ionize molecules directly from the solid state thereby reducing the chance of thermal degradation. (Two other ionization techniques have been recently developed; one by Cotter (C503) using laser desorption chemical ionization mass spectrometry and another by Vestal and co-workers (C504) using laser vaporization by very rapid heating of a liquid solution containing the sample and final vaporization by impact of an aerosol containing the sample on a heated metal plate. The latter method requires no ionizing source such as electron beam or strong electric field.) Although these methods use fundamentally different excitation sources, similarities in their mass spectra suggest a related ionization process (C3, C8, C475, C498, C505, C506).

Benninghoven and co-workers reported the first systematic study of some thermally sensitive molecules by SIMS. Their results for amino acids showed abundant [HM]$^+$ and [M – H]$^-$ molecular-like ions as well as the characteristic fragment
ion [HM – HCOOH]^+ resulting from decarboxylation of the protonated molecular ion. These mass spectral features are due to ion/molecule reactions and unimolecular dissociations which are also common in other forms of mass spectrometry, e.g., chemical ionization mass spectrometry (C475, C477, C478, C507). The basic fragmentation process involves the loss of neutral molecules from the electron-electron protonated or deprotonated molecular ion. Several detailed studies of the SIMS fragmentation process have been recently reported for amino acids (C475, C508-C511), organic acids (C512), various biomolecules (C477, C513), and organic amines and amides (C477, C514). Other recent organic SIMS studies include the analysis of sugars, nucleotides, nucleosides, and peptides (C515-C517), and mixtures of amino acids, barbiturates, amines, and amides (C518-C521). Similar results reported in recent FAB studies of amino acids, peptides, nucleotides, alkaloids, saccharides, and many other biomolecules (C161-C167). In fact, most FAB applications to date deal with biomolecules (C5, C497).

In addition to the protonated molecular ion, [HM]⁺, the SIMS spectra of organic molecules contain cationized species formed between the molecule and metal (alkali, transition or noble) ions from the substrate or impurities (C475, C477). Cooks and co-workers tested the cationizing ability of several metals with both polar and nonpolar organic molecules and found that (1) the cationization yield varied for different metals and for metals in different charge states, (2) the site of attachment is dependent on the nature of the metal, and (3) the degree and type of fragmentation is dependent on the attachment site and the proximity of the interaction between the atom and the organic molecule (C475, C477). Recent examples of cationization in SIMS include studies on amino acids (C475, C508-C511), organic acids (C512), and organic amines and amides (C477, C514).

The polarity of the organic molecules affects the fragmentation reaction. While polar molecules form intense cationized species and exhibit fragment ions characteristic of even-electron ions, nonpolar molecules form intense M⁺ ions (and another possibility, the benzoyl cation, see below). Subsequent fragmentation of the M⁺ ion is comparable to E1 (electron impact) results. Hence, the chemical properties of molecules affect the formation of molecular ions. Empirical rules for cationization can perhaps be based on known principles of coordination chemistry (C529).

Cationization in other forms of mass spectrometry such as field desorption (FD), plasma desorption (PD), and laser desorption (LD) usually occurs by alkali ion attachment (C486-C487). Cooks and co-workers (C529), however, combined for the first time, laser desorption with mass spectrometry/mass spectrometry showing cationization of sucrose by chloride acts as a room-temperature isolation matrix from ported.

The secondary ion intensity for the organic salts is generally around 2 orders of magnitude higher than that observed in cationization. The efficiency of the various ionization processes in organic SIMS, therefore, falls in the order direct emission > cationization > electron transfer. The higher efficiency of the direct emission process lowers the detection limits for organic ions in SIMS such that picogram quantities can be detected (C535).

**LITERATURE CITED**


**R-XRAY PHOTOELECTRON SPECTROSCOPY (XPS)**

