

I. AUGER ELECTRON SPECTROSCOPY

1. Introduction

The Auger electron spectroscopy technique for chemical analysis of surfaces is based on the Auger radiationless process. When a core level of a surface atom is ionized by an impinging electron beam, the atom may decay to a lower energy state through an electronic rearrangement which leaves the atom in a doubly ionized state. The energy difference between these two states is given to the ejected Auger electron which will have a kinetic energy characteristic of the parent atom. When the Auger transitions occur within a few angstroms of the surface, the Auger electrons may be ejected from the surface without loss of energy and give rise to peaks in the secondary electron energy distribution function. The energy and shape of these Auger features can be used to unambiguously identify the composition of the solid surface.

An Auger electron spectroscopy system consists of an ultrahigh vacuum system, an electron gun for specimen excitation, and an energy analyzer for detection of Auger electron peaks in the total secondary electron energy distribution. Because the Auger peaks are superimposed on a rather large continuous background, they are more easily detected by differentiating the energy distribution

function $N(E)$. Thus the conventional Auger spectrum is the function $\frac{dN(E)}{dE}$. Electronic differentiation is readily accomplished with a velocity analyzer by superimposing a small a.c. voltage on the energy selecting voltage and synchronously detecting the output of the electron multiplier. The peak-to-peak magnitude of an Auger peak in a differentiated spectrum generally is directly related to the surface concentration of the element which produces the Auger electrons. Quantitative analysis may be accomplished with varying degrees of accuracy by comparing the peak heights obtained from an unknown specimen with those from pure elemental standards or from compounds of known composition.

The sensitivity of the Auger technique is determined by the transition probability of the Auger transitions involved, the incident beam current and energy, and by the collection efficiency of the analyzer. With a 3 kV, 50 μ A beam and a high sensitivity cylindrical mirror analyzer, the limit of detection for the elements varies between approximately 0.02 and 0.2 atomic percent with spectrum scanning rates of 1 eV per second. All elements above helium produce Auger peaks in the 0-2000 eV range.

2. Experimental Techniques Used to Obtain Standard Auger Spectra

The experimental arrangement for obtaining the Auger spectra is shown in Figure 1. Several specimens were mounted on the carousel holder at each loading and sequentially rotated into the analysis position. The analysis was carried out with the excitation beam normal to the specimen surface except for some nonconducting specimens where grazing incidence was required to reduce charging effects. In these cases the angle of incidence was 60° for both the specimen and the silver standard used to set the operating parameters.

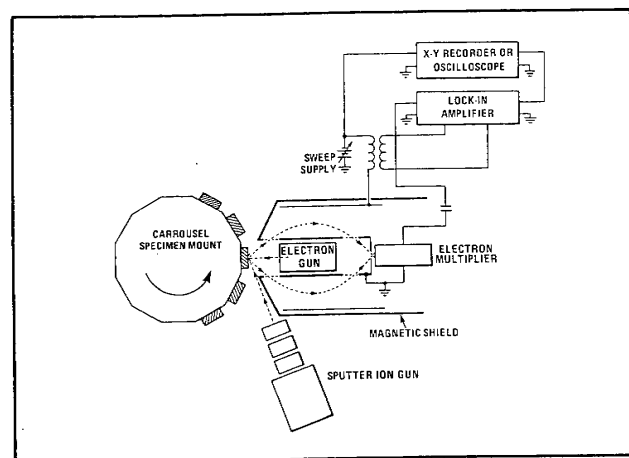


Figure 1: Schematic of the experimental arrangement used for obtaining standard Auger spectra.

The procedures used to obtain clean specimens were argon ion sputter-etching, scribing, and thin film deposition. Most spectra were taken during argon ion sputtering which produced relatively

clean surfaces without baking the system. The sputter-etching rates were considerably faster than the adsorption rate of active residual gases.

For many of the highly reactive metals the surface oxide layer was too thick for convenient removal by sputter-etching. A more expedient method for producing a clean surface was to scribe the surface in situ with a carbide tip. The top of the scratched groove was wide enough to allow the incident electron beam to excite only the freshly exposed material. Even with the high speed cylindrical analyzer, considerable adsorption sometimes occurred before completion of the measurement. The high vapor pressure of many of the reactive metals prevented attainment of ultrahigh vacuum through bakeout. The spectrum from magnesium was obtained from a freshly evaporated film, and the cesium and argon spectra were obtained by implanting Cs and Ar ions in a silicon wafer. The xenon spectrum was obtained by implanting Xe ions in a carbon specimen.

The energy scale was calibrated by measuring the analyzer voltage required to transmit elastically reflected primary electrons of known energy. After reflection from the target surface into the analyzer, the kinetic energy of the primary electron is:

$$E_k = eV_p + \phi_f - \phi_a \quad (1)$$

where V_p is the electron gun voltage, ϕ_f is the electron gun filament work function and ϕ_a is the work

function of the analyzer material. The analyzer voltage required to transmit the elastically reflected electrons is:

$$eV_o = \alpha E_k = \alpha(eV_p + \phi_f - \phi_a) \quad (2)$$

where α is a constant determined by the geometry of the analyzer. The measured α is V_o/V_p while the actual α is given by (2). Thus the percentage error due to work functions in this procedure is:

$$\frac{\Delta\alpha}{\alpha} = \frac{\phi_a - \phi_f}{eV_p} \quad (3)$$

The difference between the work functions of the stainless steel analyzer and the tungsten filament is expected to be less than 1 eV. For a gun voltage of 2,000 volts the percentage error caused by work functions is therefore less than 0.05%. The accuracy of the measured gun voltage was better than one volt at 2,000 volts. Thus, for the energy range from zero to 2,000 eV, the instrumentation accuracy of the data presented here is about 1 eV.

The amplitude of the Auger signal is dependent on the exciting beam energy and current, the transmission and resolution of the analyzer, the amplitude of the modulation voltage, the multiplier gain, and the sensitivity setting of the lock-in amplifier. For meaningful comparison of the spectra from various elements, it is necessary to record these variables.

The analyzer transmission and resolution were 10% and about 0.6% respectively for all data in this handbook.

Beam energies of 3 and 5 keV were used to obtain the Auger spectra in this handbook. The appropriate value of excitation energy is indicated on each

spectrum. Beam current ranged from 2 μ A to 50 μ A and was adjusted to provide convenient measurement conditions but was kept low enough to avoid specimen damage.

The multiplier gain was kept at a constant value by adjusting the multiplier voltage to maintain a constant peak-to-peak deflection for the 351 eV Ag peak when using standard values for all other parameters.

The amplitude of the modulation voltage used depended on the energy width of the Auger peaks. The instrumental contribution to the peak width increases linearly with energy in velocity analyzers. Thus for a resolution of 0.6% the instrumental contribution is 6 eV at 1,000 eV and 12 eV at 2,000 eV. The amplitude of the perturbing voltage ranged from 2 eV at low energies up to 6 eV at high energies. In all cases care was taken to insure that the peak shapes were not distorted by overmodulation. Within this limit the amplitude of the Auger signal is proportional to the modulation amplitude.

After adjusting the multiplier voltage to achieve a standard signal from Ag, only the lock-in amplifier gain, modulation amplitude and incident beam energy and current were adjusted to obtain spectra from other samples. The scale factors which label each of the spectra in this handbook represent the increase in instrumental sensitivity relative to that used to obtain the Ag spectrum with 3 keV excitation.

The procedure used to normalize the multiplier gain does not properly account for the variation in first stage gain with energy. The first stage is normally at ground potential which means that the Auger electrons strike the first stage with their

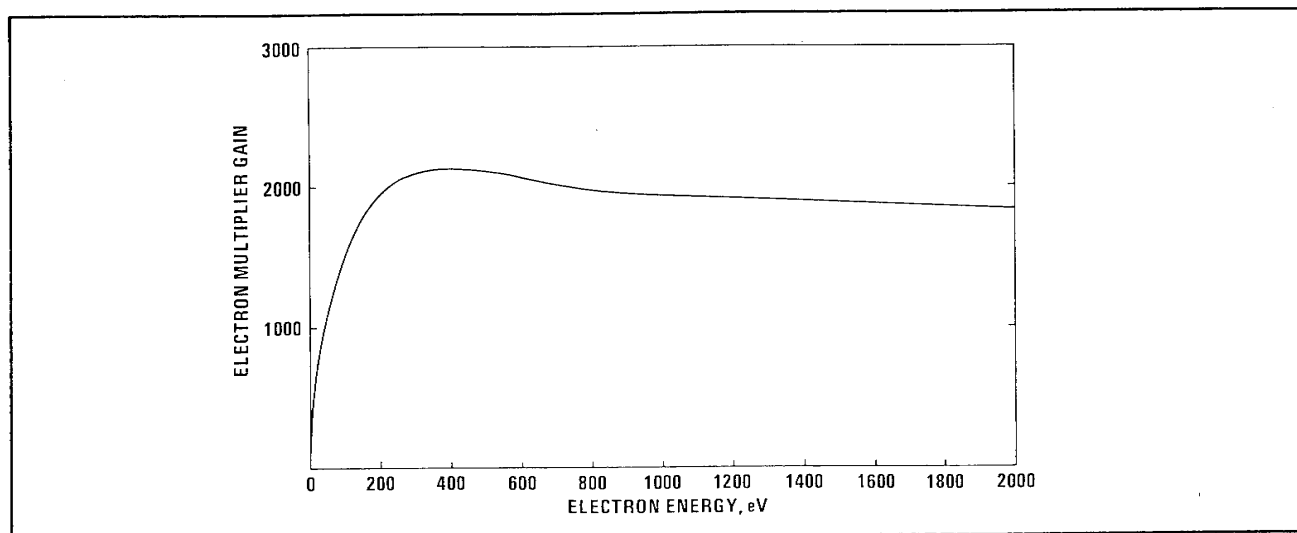


Figure 2: Typical electron multiplier gain variation with electron energy.

initial energy. The multiplier gain varies with energy according to Figure 2. The low gain at low energies is desirable in that it suppresses the large, low energy signal from the true secondary electrons. For electrons with more than 200 eV energy the gain is

nearly constant. If the energy dependence of the first stage gain varies in time, a corresponding error occurs in the scale factor. Above 200 eV, however, this error must be small, because the first stage gain in this range is nearly independent of energy.

3. Qualitative Analysis

The identification of peaks in the Auger spectrum is accomplished most efficiently through the combined use of a chart of Principal Auger Electron Energies and the standard spectra. The chart (Inside Back Cover) gives the relationship between Auger electron energies and atomic number. For

simplicity only the principal Auger peaks are listed on the chart. The KLL, LMM and MNN Auger transitions produce observable peaks which allow identification of all elements above helium by scanning the 0-2,000 eV range. Although Auger peaks from different elements can sometimes overlap,

complete obliteration of peaks from a trace impurity by more dominant species seldom occurs in practice.

A useful procedure for labeling peaks in an Auger spectrum is the following:

1. First concentrate only on the major peaks. Use the chart of Principal Auger Electron Energies to reduce the number of possibilities to two or three elements. The correct identification of major Auger peaks is then easily accomplished by referring to the standard Auger spectra. When making this comparison it must be noted that peak shifts of a few eV often occur due to chemical bonding. Therefore, deviations of a few eV in peak energy from those listed on the standard spectra should be considered insignificant if the element in question is in a chemical environment different from that used for the standard spectrum.

2. When positive identification of major constituents has been made, use the standard spectra to label all peaks attributable to them.
3. Peaks which are not yet labeled originate from minor constituents whose identification proceeds as above. Because of low concentration, only the most prominent peaks of these elements will be observed in the spectrum.

In general, this procedure results in rapid and unambiguous interpretation of the spectra. If peaks remain which have not yet been identified, they may be energy loss peaks due to primary electrons which have lost a discrete amount of energy through ionization of core levels. To test this possibility, change the primary beam energy and observe whether the peak shifts in energy by the same amount. If the peak moves, it is not an Auger peak. To minimize the occurrence of energy loss peaks, the primary beam energy should be set well above the Auger energies of interest.

4. Quantitative Analysis

In determining the relationship between the Auger electron signal and atomic concentration it is necessary to evaluate the effect of instrumental parameters on the measured Auger signal. The important instrumental variables are the primary electron beam current (I_p), the primary beam energy (E_p) and, for the conventional $dN(E)/dE$ spectrum, the modulation energy (E_m).

The anticipated linear relationship between the Auger peak-to-peak amplitude and I_p is experimentally verified in Figure 3 for the Au (69 eV) peak. This linear relationship between Auger amplitude and incident beam current is no longer valid when the incident electron beam diameter exceeds the analyzer source diameter or when excessively high current density causes damage to the specimen.

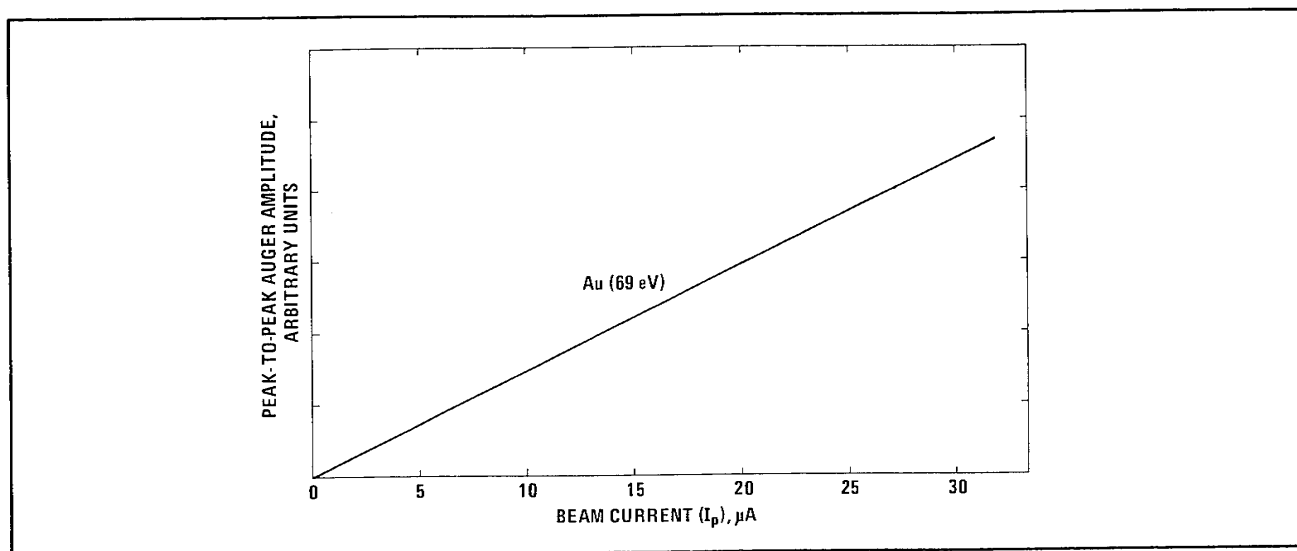


Figure 3: Verification of the linear relationship between the peak-to-peak amplitude of the Auger signal and excitation beam current for the Au(69 eV) Auger peak; $E_p = 5$ keV, $E_m = 2$ eV.

The relationship between the Auger peak-to-peak amplitudes of the Au (69 eV) and Au (2024 eV) peaks and modulation (peak-to-peak) energy, E_m , is shown in Figure 4. The Auger amplitude is proportional to the modulation energy when the modulation energy is small compared with the Auger peak width. For larger modulation amplitudes, the peak is instrumentally broadened and the peak-to-peak amplitude becomes nonlinear with E_m . As shown, the Au (69 eV) peak-to-peak amplitude is significantly nonlinear with modulation energy greater than 2 eV peak-to-peak, while, due to its larger peak width, the amplitude of the 2024 eV peak is linear throughout the zero to 6 eV range.

The variation of the Auger electron yield with primary beam energy, E_p , is largely determined by the energy dependence of the electron impact ionization cross-section of the core level involved in the

Auger transition. The Auger yield rises abruptly from zero as E_p crosses the ionization threshold, E_c , and increases to a maximum for E_p/E_c of at least five. When I_p and E_m are maintained constant, Figure 5 shows that the Au (69 eV) transition reaches maximum yield at $E_p \approx 1.5$ keV. In contrast, the higher energy Au (2024 eV) peak reaches maximum yield at a primary beam energy greater than 10 keV.

With the instrumental parameters in mind a highly useful form of quantitative analysis can be achieved with the use of elemental standards. The accuracy of the methods to be described is similar to that realized in electron microprobe analysis using methods of similar sophistication.

A first order approximation to quantitative analysis can be accomplished through comparison of the Auger signal from the sample to the Auger signal

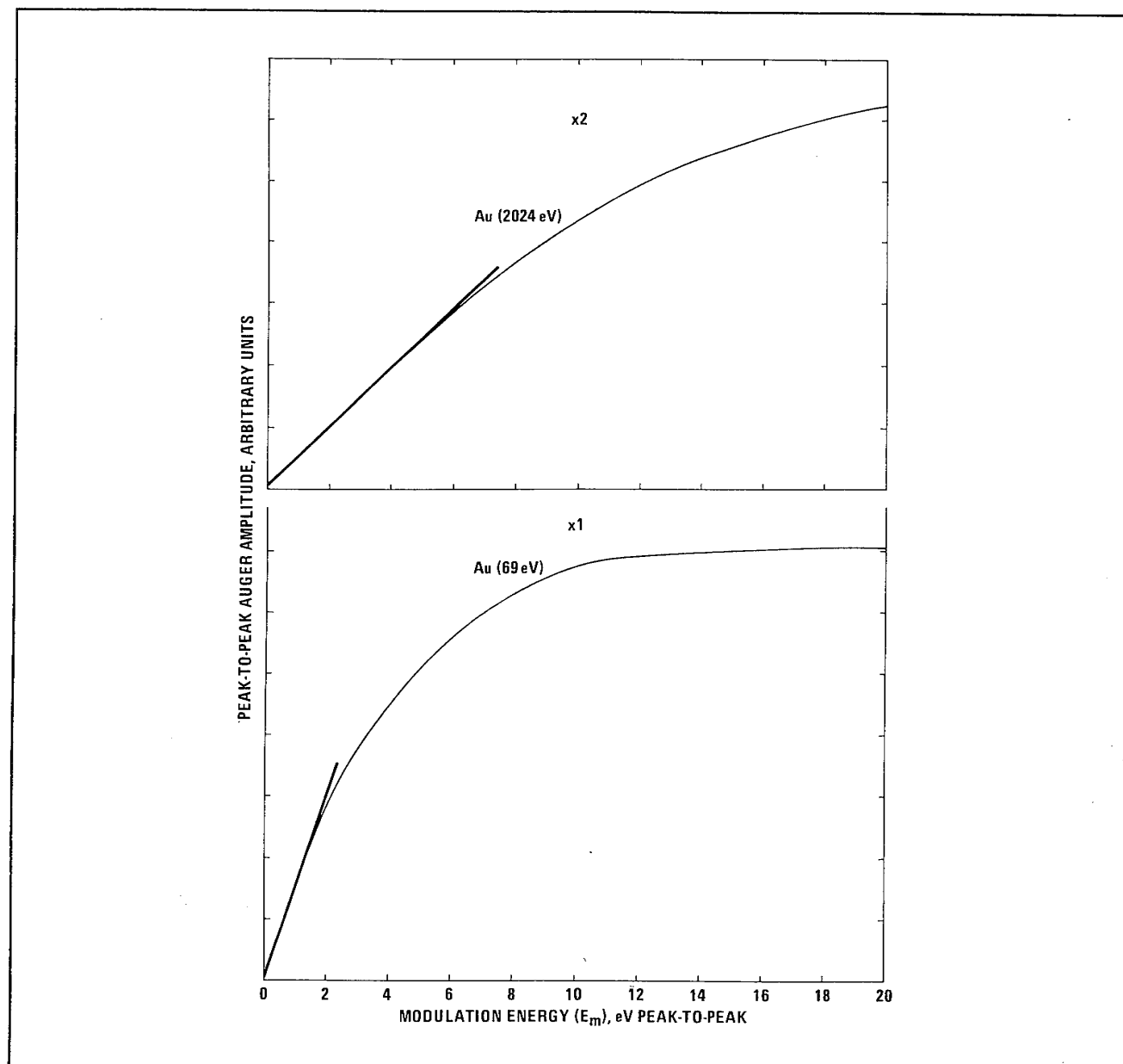


Figure 4: Relationship between Auger peak-to-peak amplitude and modulation energy for the Au(69 eV) and Au(2024 eV) peaks; $E_p = 8$ keV, $I_p = 3 \mu\text{A}$.

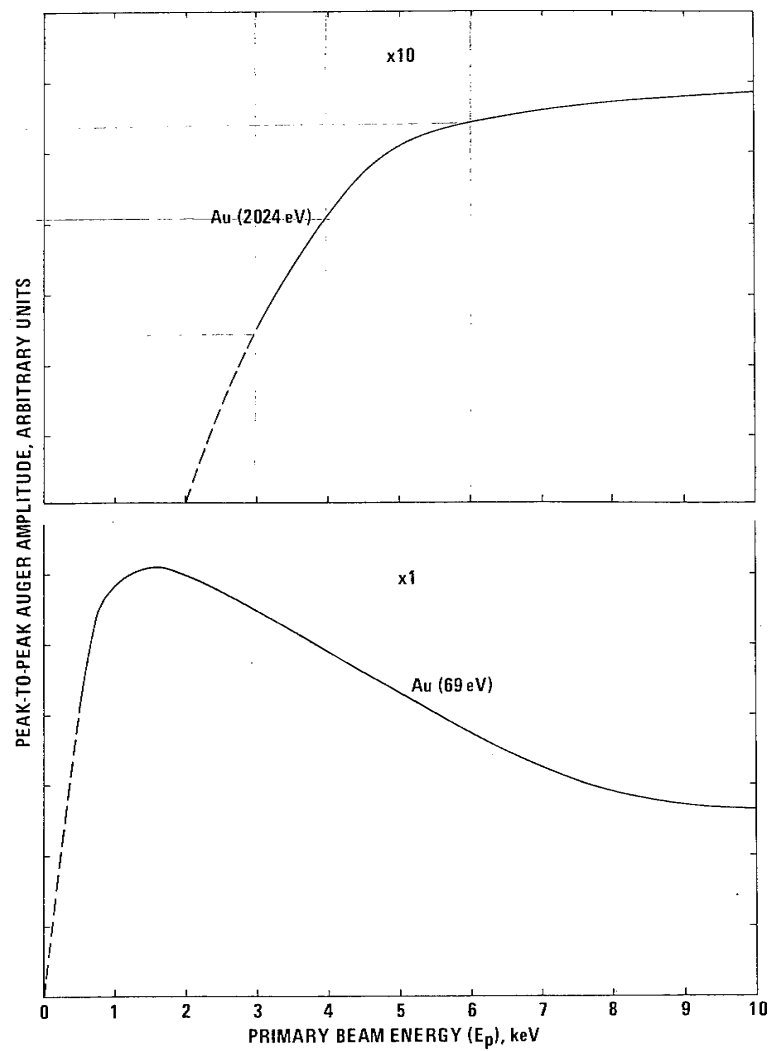


Figure 5: Dependence of Auger peak-to-peak amplitude on primary beam energy, E_p , for the Au(69 eV) and Au(2024 eV) peaks; $I_p = 2 \mu\text{A}$, $E_m = 2 \text{ eV}$ peak-to-peak.

from a pure elemental standard. In this approximation, the atomic concentration of element X in the sample is:

$$C_X = \frac{I_X}{I_{X,STD}} \quad (4)$$

where I_X and $I_{X,STD}$ are the peak-to-peak Auger amplitudes from the sample and standard respectively. For greater accuracy, a pure elemental standard should be mounted in the system with the specimen of interest. The peak-to-peak Auger signal from each sample can then be compared under identical experimental conditions. When the element of interest produces several Auger peaks, the same peak for the two specimens must be used for this comparison. It should be noted that surface layer contamination must be removed from both specimens in order to obtain true measurements of I_X and $I_{X,STD}$.

Another method, which avoids the need for a large number of pure elemental standards, is to compare the signal from the specimen with that from a pure silver target. The relative sensitivity, S_X , between any element, X, and silver can be obtained from the standard Auger spectra in this handbook using:

$$S_X(E_p) = \left(\frac{A+B}{A} \right) \frac{I_X^H}{K_X I_{Ag}^H} \quad (5)$$

where I_X^H and I_{Ag}^H are the peak-to-peak amplitudes from the handbook spectra of element X (with the desired E_p) and silver, respectively. K_X is the handbook scale factor ($K_{Ag} = 1$) printed above the portion of the spectrum of interest. A and B are the chemical formula indices of compound $X_A Y_B$ and are used to make a first order correction for the

density of atom X in the analysis volume. A more accurate correction can be made by using the ratio of the number density of X atoms in its elemental state to the number density of X atoms in the compound.

To determine the atomic concentration with this technique, E_p should be set at the value used for the handbook data and E_m should be low enough to prevent significant distortion due to excessive modulation. Without changing the electron multiplier voltage or E_p (vary only I_p , E_m , and lock-in sensitivity), the spectrum is obtained from the test specimen. The atomic concentration of element X is, then:

$$C_X = \frac{I_X}{I_{Ag} S_X D_X} \quad (6)$$

where I_X is the peak-to-peak amplitude of the element X from the test specimen, I_{Ag} is the peak-to-peak amplitude from the Ag standard and D_X is a relative scale factor between the spectra for the test specimen and silver. If the lock-in amplifier sensitivity, L_X , modulation energy, $E_{m,X}$, and primary beam current, $I_{p,X}$ settings used to obtain the test spectrum are different from those of the Ag spectrum (i.e. L_{Ag} , $E_{m,Ag}$ and $I_{p,Ag}$) the relative scale factor is:

$$D_X = \frac{L_X E_{m,X} I_{p,X}}{L_{Ag} E_{m,Ag} I_{p,Ag}} \quad (7)$$

When elemental or silver standards are not used, it is possible to express the atomic concentration as:

$$C_X = \frac{I_X}{S_X d_X} \bigg/ \sum_{\alpha} \frac{I_{\alpha}}{S_{\alpha} d_{\alpha}} \quad (8)$$

where I_X and S_X are defined as before, the summation is over one peak per element and d_X is the scale factor defined by:

$$d_X = L_X E_{m,X} I_{p,X} \quad (9)$$

To facilitate the use of the latter method, relative elemental sensitivity factors $S_X(E_p)$ of the more useful transitions obtained at $E_p = 3, 5$, and 10 keV are presented in graphical form in section I.5 below. In each case, S_X values obtained from spectra of elemental or compound standards are relative to the Ag (351 eV) peak in the handbook according to equation (5). The data have been normalized so that $S_{Ag} = 1$ with $E_p = 3$ keV.

As an example of how the relative sensitivity factors are to be used, equation (8) was applied to Auger peak-to-peak amplitudes of a ductile fracture surface of 304 stainless steel. Such a surface prepared in situ in a UHV environment exhibits the bulk composition of the material. Since the low energy Auger peaks are generally more susceptible to distortion by magnetic effects and localized specimen charging it is best to use peaks occurring above about 100 eV for quantitative analysis. Therefore, the Fe(703 eV) peak rather than the Fe(47 eV) peak was chosen in this example and as shown in Figure 6, the relative peak amplitudes of the Fe(703 eV), Cr(529 eV), and Ni(848 eV) peaks were 10.1, 4.7 and 1.5 respectively (in any

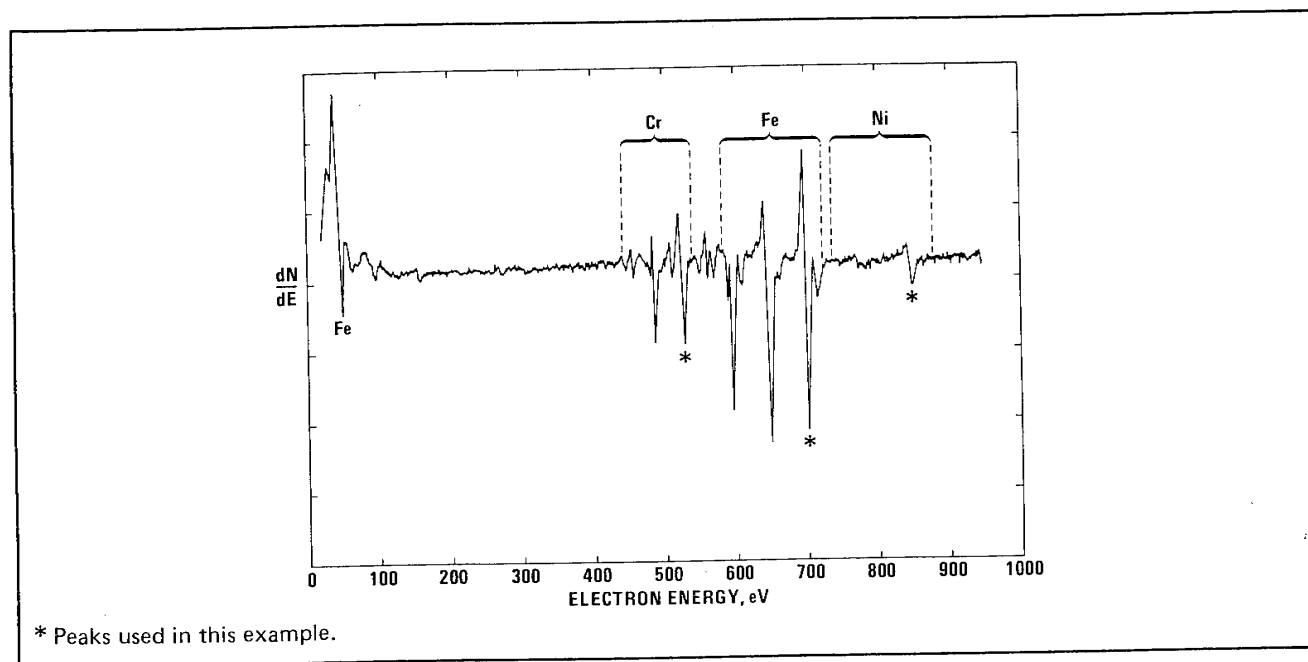


Figure 6: Auger spectrum from ductile fracture surface of 304 stainless steel used to illustrate quantitative Auger analysis; $E_p = 3$ keV, $E_m = 4$ eV peak-to-peak, $I_p \approx 2 \mu A$.

arbitrary units). The relative sensitivity factors, for these peaks calculated using equation (5) are 0.20, 0.29 and 0.27, respectively. The scale factor d_X is the same for all peaks and therefore cancels out. Application of equation (8) to the Fe(703 eV) peak in this specimen yields:

$$C_{Fe} = \frac{10.1/.20}{10.1/.20 + 4.7/.29 + 1.5/.27} = 0.70$$

Similar calculations applying equation (8) to the Cr(529 eV) and Ni(848 eV) peaks give: $C_{Cr}=0.22$ and $C_{Ni} = 0.08$. The known bulk concentrations of this alloy are $C_{Fe} = 0.702$, $C_{Cr} = 0.205$ and $C_{Ni} = 0.093$ which compare favorably with surface concentrations obtained from the Auger data.

There are several inherent errors in these simple quantitative techniques. These are: (1) matrix effects on electron escape depths and backscattering factors, (2) chemical effects on peak shapes, and (3) surface topography. For example, the dependence of Auger electron escape depth on the electronic structure of the host material may alter

the depth of measurement in the specimen relative to that in a standard. Since the magnitude of the Auger signal is proportional to the number of atoms in the analysis volume, a larger escape depth will cause a corresponding increase in Auger signal (as long as the element of interest is distributed throughout the escape depth layer). Chemical effects can change the peak shape and thus lead to error when using peak-to-peak heights in the differentiated spectrum for a measure of the Auger signal. Generally, a highly polished surface produces a larger Auger signal than a rough surface. This effect is minimized by determining concentrations from equation (8) since surface roughness is expected to decrease all Auger peaks by nearly the same percentage.

When highly accurate quantitative analysis is desired, standards of known concentrations which are close to that of the actual specimens should be used. In this way, electron escape depths, backscattering factors, and chemical effects are similar in both samples.

5. Relative Elemental Sensitivity Factors

The relative elemental sensitivity factors, S_X , presented graphically in the following pages were obtained from pure elements and compounds using primary beam energies of 3, 5, and 10 keV. As discussed in the Quantitative Analysis Section (I.4),

the atomic concentration of element X may be obtained from equations (6) or (8) using S_X values. The S_X values plotted here have been identified with specific transitions in the Handbook spectra and are appropriate only for those transitions.

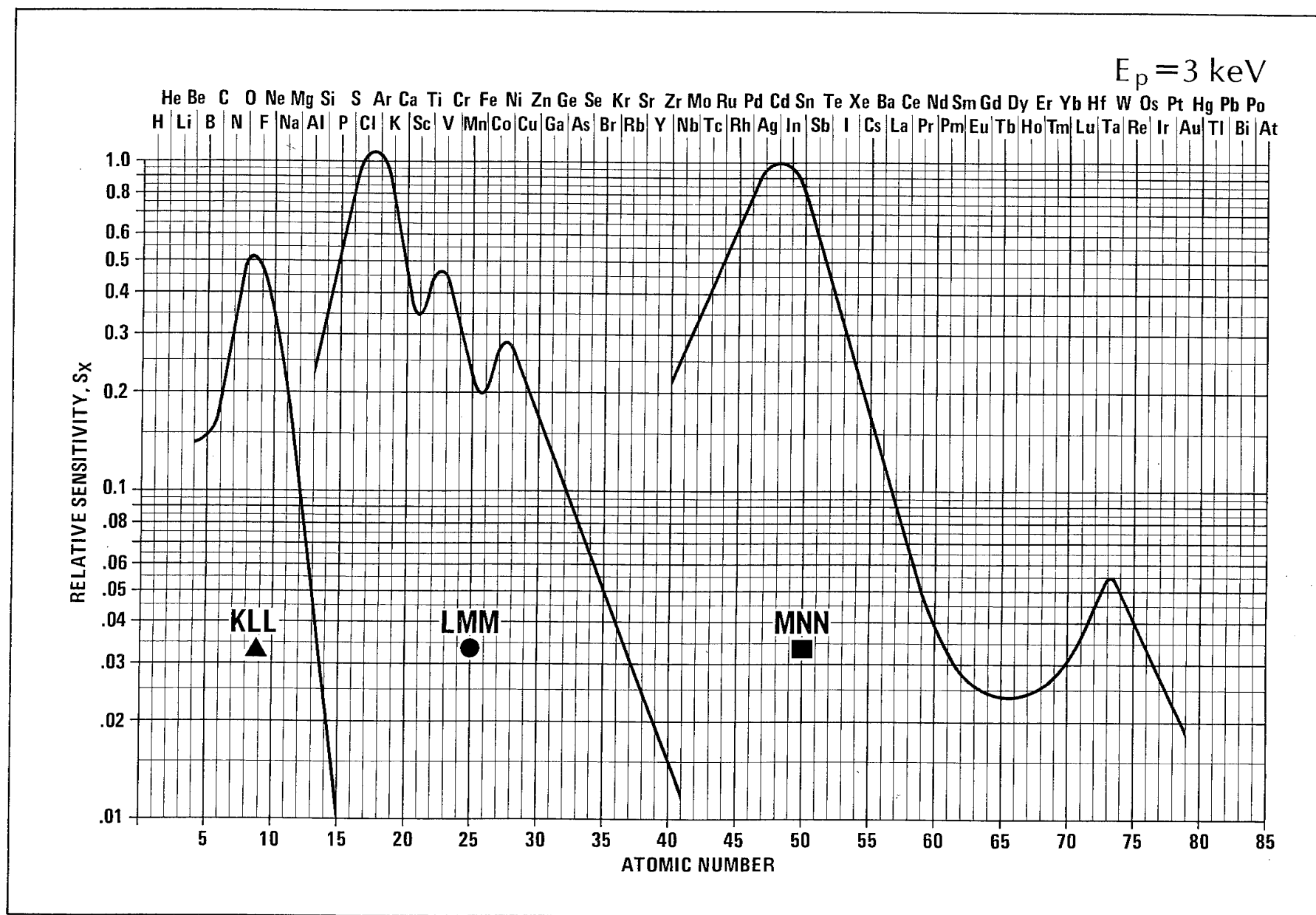
Peaks used to calculate the sensitivity curves of KLL transitions are marked on the spectra by ▲; those used for the LMM transitions by ●; and those used for the MNN transitions by ■. The peaks for which S_X values are plotted are those normally used to detect and determine concentrations of the elements. The sensitivity factor for any other peak in the Handbook may be obtained using equation 5.

Higher energy (>100 eV) transitions have been emphasized because these peaks are less subject to distortion by magnetic field and sample charging effects. In some cases average values of S_X were used. For example, three measurements were obtained for the Fe(703eV) peak at $E_p = 3$ keV. The S_{Fe} value plotted is the average of these measurements and is within $\pm 5\%$ of the measured values. Larger uncertainties (about $\pm 20\%$) are expected in S_X values for elements obtained from insulating standards.

Also a few of the 5 and 10 keV values were estimated from the 3 keV values and data on the dependence of the sensitivity on excitation energy. For example the sensitivity factor for the lutetium (1573 eV) peak can be estimated from the 3 keV lutetium data using the peak-to-peak height ratio for the silicon (1619 eV) peak at 3 and 5 keV.

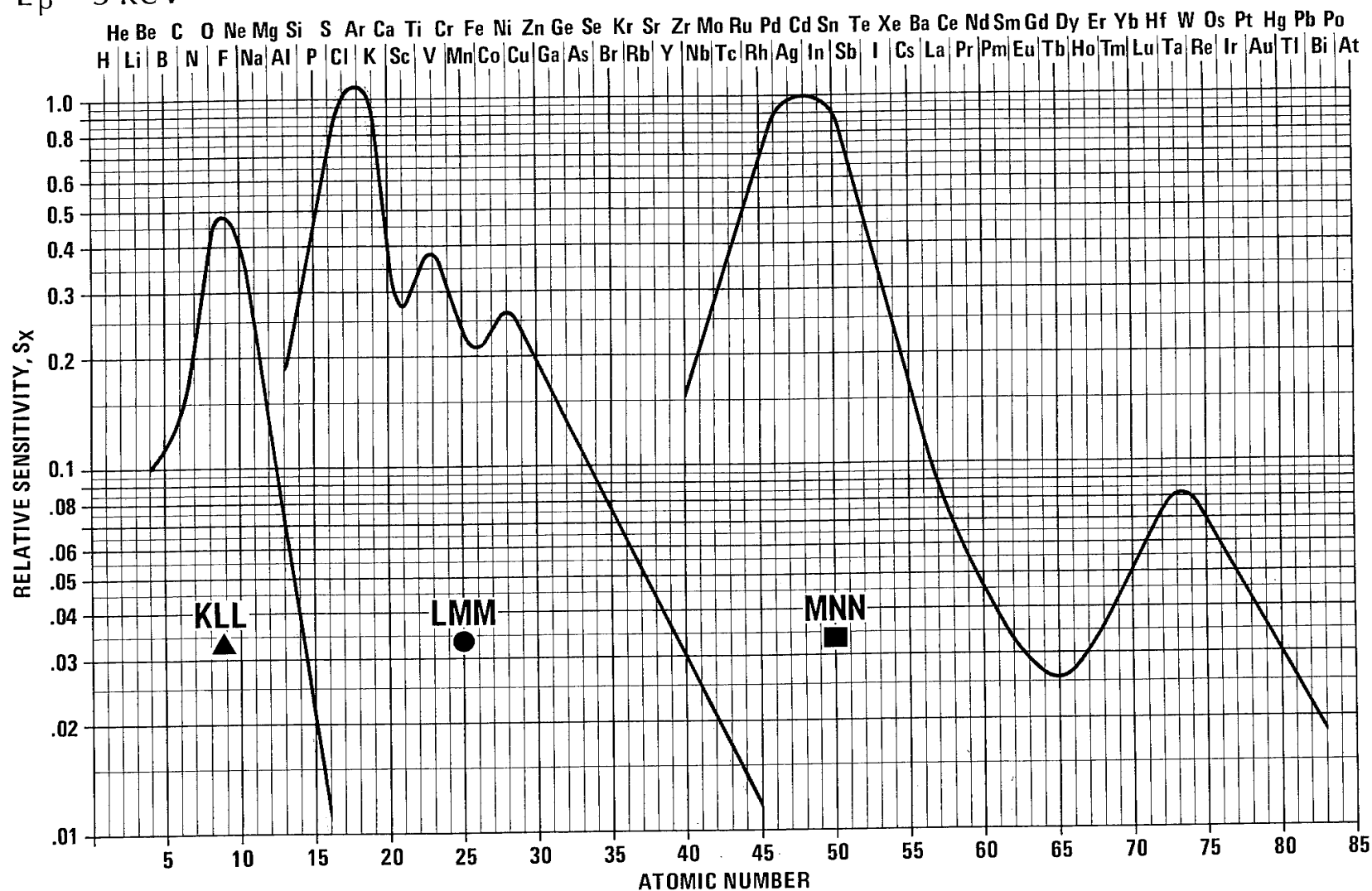
The curves presented below should be considered a "best fit" to average and interpolated values and will not necessarily be identical with sensitivity factors calculated directly from handbook spectra. An estimate of the accuracy of the plotted S_X values is shown by the shaded areas surrounding the solid curves in the graphs. The relative elemental sensitivity factors in this section are not suggested as replacements for internal standards. A higher degree of accuracy can be achieved by using a standard with a chemical matrix similar to that of the test specimen.

Relative Auger Sensitivities of the Elements

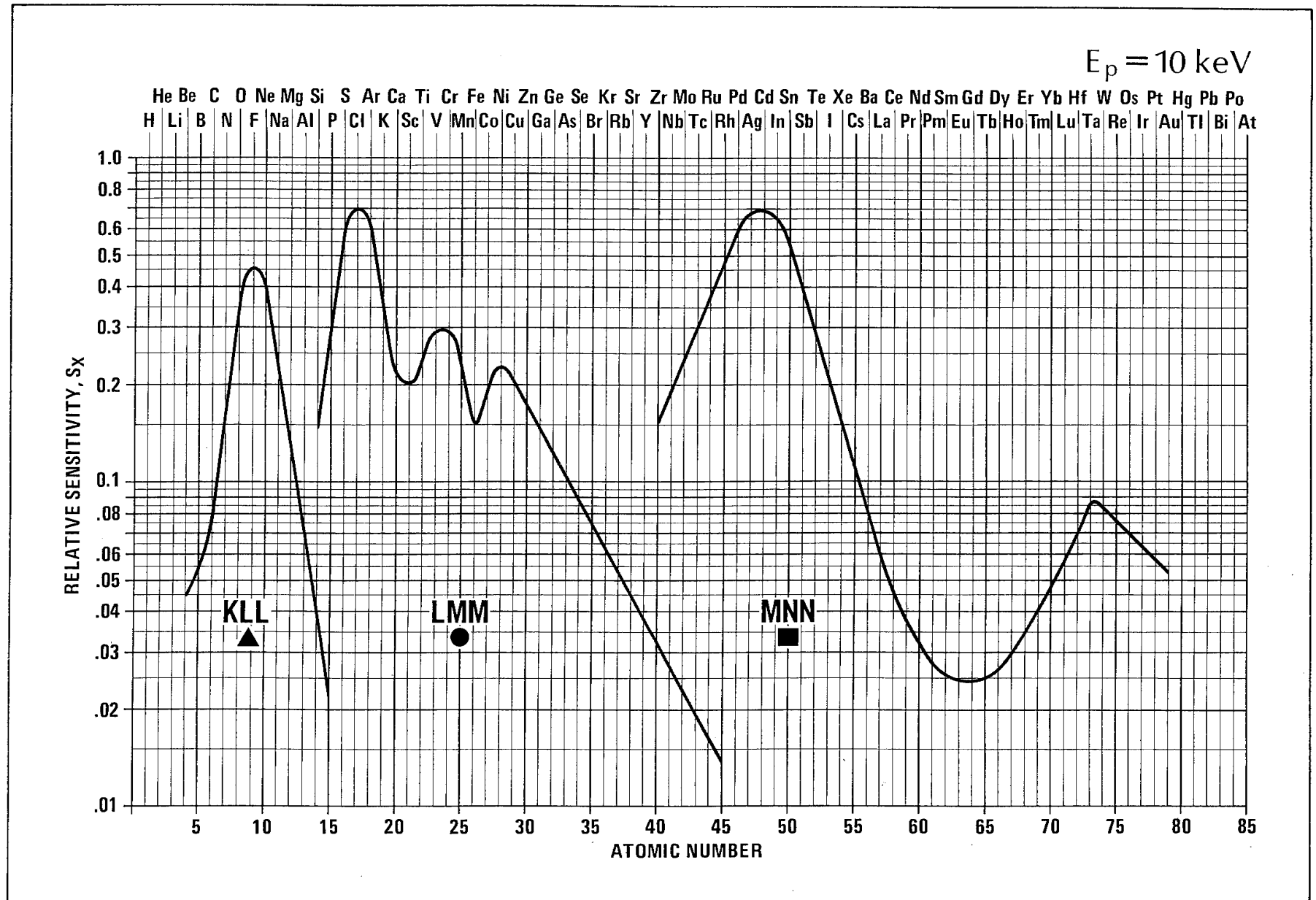


Relative Auger Sensitivities of the Elements

$E_p = 5 \text{ keV}$



Relative Auger Sensitivities of the Elements



6. Chart of Principal Auger Electron Energies — Description

The PHI Chart of Principal Auger Electron Energies (Inside Back Cover) indicates the relationship between the energies of the principal observed Auger transitions and atomic number. The dots indicate experimental values of the energies at which principal negative peaks occur in the Auger spectrum. The large dots indicate the most intense peaks obtained from each element. These are the peaks normally used for quick identification of the

elements. The Auger transitions which give rise to the observed peaks are also indicated. For example, a KLL transition involves initial ionization of the K shell and relaxation of an electron from the L shell into the K vacancy. Energy released in this process is transferred to another L electron which is consequently ejected from the specimen with characteristic energy and can be identified as an Auger electron.

7. Standard Auger Spectra of the Elements — Description

The spectra presented in this handbook were obtained from pure elemental materials or from compounds of known composition. The sensitivity of the instrument, relative to that used to obtain the silver spectrum with 3 keV excitation is indicated by scale factors on each graph. The energy, E_p , of the electron beam used for excitation is also indicated since spectra obtained using 5 keV as well as 3 keV excitation are included when they

provide information not contained in the 3 keV spectra.

For spectra from elemental standards, the energy of each peak is labeled on the graph. Following conventional procedures, the numbers indicate the energies of the negative peaks in the Auger spectrum. When a peak originates from an impurity, the chemical symbol of that impurity is used to

label the peak. For compound standards, the transitions due to the element under consideration are labeled by chemical symbol and energy while other constituents and impurities are labeled by chemical symbols only. The compound used is indicated on these spectra.

The peaks in each spectrum that were used to determine the S_X values plotted in Section I.5 are

marked by ▲, ● or ■ respectively depending on whether the data fall in the KLL, LMM, or MNN segment of the S_X curves.

The energy scale is broken on many of the spectra to expand the low energy region and also include the high energy transitions. When an intermediate energy range is not recorded, no transitions of significant amplitude were present in that range.

8. How to Use This Handbook

The Handbook of Auger Electron Spectroscopy can be of greatest aid to the Auger spectroscopist when used according to the following procedures:

Qualitative Analysis:

Identification of species present can be most readily accomplished using the combination of the Chart of Principal Auger Electron Energies (Inside Back Cover) and the standard spectra as follows:

1. Concentrating only on major peaks, use the chart to reduce the number of possibilities to two or three elements.
2. Make positive identification of major constituents by referring to the standard spectra of the elements in question.
3. Label all peaks from dominant species.
4. Peaks which are not yet labeled originate from minor constituents whose identification proceeds as in steps 1 and 2 above. Because of low concentration, only the most prominent peaks of these elements will be observed in the spectrum.

Quantitative Analysis:

Quantitative information can be obtained using the standard spectra and a clean silver target as follows:

1. Calculate the relative sensitivity, S_X , between the element X of compound $X_A Y_B$ and silver from the Auger spectra in this handbook using:

$$S_X(E_p) = \left(\frac{A+B}{A} \right) \frac{I_X^H}{K_X I_{Ag}^H} \quad (5)$$

I_X^H and I_{Ag}^H are the peak-to-peak amplitudes of one peak in the handbook spectra for element X and silver respectively.

K_X is the scale factor on the handbook spectrum for element X.

2. Calculate the atomic concentration of element X using:

$$C_X = \frac{I_X}{I_{Ag} S_X D_X} \quad (6)$$

I_X and I_{Ag} are the peak-to-peak heights from the spectra of element X on the specimen and the pure silver target respectively and D_X is the scale factor as defined in equation (7) in section I.4 above. Note that the same pair of Auger peaks must be used to calculate C_X as were used to calculate S_X .

3. Approximate relative elemental sensitivity factors, S_X , have been listed in section I.5 of

this handbook. These sensitivity factors can be used in lieu of the reference standard, as suggested in equation (8). However, it is again pointed out that the quantitative limitations of this technique can be severe (See section I.4 on quantitative analysis). The handbook spectra have been marked to indicate which peaks were used to obtain the elemental sensitivity factor curves in section I.5.