Conf. 740429--1

(Paper to be presented at International Conference on Electron Spectroscopy, Namur, Belgium, April 1974 (to be published in J. of Electron Spectroscopy)).

EXPERIMENTAL EVALUATION OF A SIMPLE MODEL FOR QUANTITATIVE ANALYSIS IN X-RAY PHOTOELECTRON SPECTROSCOPY*

W. J. CARTER[†] and G. K. SCHWEITZER University of Tennessee, Knoxville, Tennessee 37916 and THOMAS A. CARLSON Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

SUMMARY

A simple model is described for calculating the relative intensities of photoelectron peaks for the different elements in a homogeneous solid sample. Using photoelectron cross sections of Scofield for Al and Mg K α x rays, we have determined the relative intensities of photoelectron peaks for various core subshells of all the elements from Z = 3 to 92. The calculated values are compared with experimental values for both gases and solids, and agreement is found to be satisfactory. Some of the special problems in quantitative analysis using x-ray photoelectron spectroscopy are discussed. In particular, it is shown how information regarding surface inhomogeneity may be obtained from comparison of intensities of photoelectron peaks.

INTRODUCTION

The use of x-ray photoelectron spectroscopy has developed in recent years into an important analytical tool. It is frequently known by the acronym ESCA (electron spectroscopy for chemical analysis). By the use of monochromatic x rays (for example, Al and Mg K α x rays of respectively 1487 and 1254 eV) photoelectrons can be ejected from the core shells of atoms. An electron spectrometer may be used to determine the kinetic energy of these photoelectrons, from which measurement the binding energies can be evaluated. Since the core binding energies are characteristic of the atom, x-ray photoelectron spectroscopy provides a means for elemental analysis.

DISTRIBUTION OF THE OCCOMPTENT IS UNLIMITED

this report was prepared as an account of wo consorted by the United States Government, Neith e Unitad States nor the United States States Atomic Ener and and the States and their employees, nor any effection or any of their employees, nor any effective subcontrators, or their employee states any warranty, express or implied, or their gal liability or responsibility for the accuracy, con eteness or usedintess of any information, apparation oulded or process disclosed, or rights.

Research sponsored jointly by the U. S. Atomic Energy Commission under contract with Union Carbide Corp., and by the University of Tennessee.

[†]Supported by Oak Ridge Associated Universities fellowship.

W.J. CARTER, G.K. SCHWEITZER, THOMAS A. CARLSON

ESCA has three important properties: (1) It can measure any element that has a core shell, which is to say all elements of Z > 2. (2) The ejected photoelectrons have a small mean-free-path in solids, the order of 10 to 20 Å, and thus the analysis deals with the surface and near surface layers of solids. (3) Changes in the chemical environment cause slight shifts in the binding energy of the core shell electrons. These shifts can be interpreted in terms of the electrostatic potential that surrounds each atom, which in turn is related to the oxidation state and nature of the chemical bonding.

Though much attention has been paid to the photoelectron energies and their use in qualitative analysis, there has been relatively only a small effort expended in using the intensities of the photoelectron peaks for quantitative analysis [1,2,3]. By means of a simple model we have employed recent calculations of Scofield [4] on atomic photoelectron cross sections to determine the relative atomic percent from photoelectron spectra of a homogeneous solid. This has been carried out for all elements from Z = 3 to 92 for both Al K α and Mg K α x rays.

DISCUSSION AND RESULTS

Simple model for quantitative analysis

Figure 1 shows schematically the basic problems involved in the use of x-ray photoelectron spectroscopy for quantitative analysis. First, it must be realized that the mean-free-path for kilovolt x rays in matter is several orders of magnitude greater than for the ejected photoelectrons. Thus, the depth to which the sample is studied is determined by the probability for an electron escaping without inelastic collisions, and the x-ray beam is essentially unattenuated over the escape depth. The probability for photoejecting an electron from a given subshell per unit volume is

$$N_{0} = \sigma n F$$
(1)

where σ is the photoelectron cross section for a given subshell of a given element, F is the x-ray flux and n is the concentration of the element in terms of atoms per unit volume.

Second, the angular distribution of the photoelectron needs to be considered. This is given by

$$N(\theta) = 1 + \beta/2 (3/2 \sin^2 \theta - 1)$$
 (2)

where θ is the angle between the direction of the photon beam and the



Some Considerations in the ESCA Study of Solids.

Fig. 1. Schematic representation of problems involved in quantitative evaluation of x-ray photoelectron spectroscopy of solids. See text for description of symbols. If sample is homogeneous without contamination $-\frac{d}{\lambda^{*}} = 1$.

direction of the ejected photoelectron. The angular parameter, β , can vary from -1 to +2 and is dependent on the photoelectron energy and the nature of the atomic orbital. Manson [5] has made comprehensive calculations of β as a function of element. At higher photoelectron energies this value approaches an asymptotic value for a given angular momentum, and corrections for relative intensities measured at a fixed angle are not large. For example, the total integrated intensities to that measured at 90° is about 10% higher for p orbitals than for s orbitals. In solids the angular correction is reduced by the leveling effect of elastic collisions. To remove the angular effect, one may measure the intensity at 54.7°, at which angle the intensity is independent of β . Our simple model assumes that any problem related to angular distribution has been corrected.

Third, the probability for escape of the electron from the material must

-3-

W.J. CARTER, G.K. SCHWEITZER, THOMAS A. CARLSON

be considered. It requires that the photoelectron emerges without any energy loss due to an inelastic collision, passes through the spectrometer and is detected. The intensity is thus equal to

$$dN = N_{G} e^{-X/\lambda} dx \cdot S$$
 (3)

where $1/\lambda$ is the reciprocal of the mean-free-path or the cross section for inelastic scattering, x is the distance below the surface, and S is the spectrometer factor. The total signal integrated from the surface to an infinite depth is

$$N = \int_{0}^{\infty} N_{0} e^{-x/\lambda} dx \cdot S = \lambda \cdot \sigma n F \cdot S.$$
 (4)

The relative intensity for two different photoelectron peaks from the same sample is

$$\frac{N_{1}}{N_{2}} = \frac{\sigma_{1} n_{1} \lambda_{1} S_{1}}{\sigma_{2} n_{2} \lambda_{2} S_{2}}.$$
 (5)

The mean-free-path, λ , for inelastic scattering is a monotonic function of the kinetic energy, \mathcal{E} , of the ejected photoelectrons. The details are complex and depend on such parameters as the plasmon frequency of the material through which the electron travels. However, over the range of interest to ESCA (100 to 1500 eV) λ can be approximately fitted to the dependence

both from theory [6] and from experiment [7].

For a given spectrometer the spectrometer factor will be the same except for a possible dependence on the kinetic energy of the ejected electron. This energy dependence can usually be determined. In our spectrometer, which is an electrostatic analyzer without predecelleration, the intensities need only be corrected by dividing by the window width, \mathcal{E} . Our simple model for quantitative analysis in ESCA assumes that the energy dependence of the spectrometer coefficient has been accounted for, and $S_1 = S_2$. The object of the calculation is to obtain the expected intensities in the photoelectron spectra for equal atomic concentration, so that $n_1 = n_2$. The choice of element and subshell for a standard is arbitrary and we have chosen the C(1s) peak. The final form of the calculation thus becomes

$$\frac{N_{Z,n\ell}}{N_{C,ls}} = \frac{\sigma_{Z,n\ell}}{\sigma_{C,ls}} \frac{\sqrt{hv - E_B(Z,n\ell)}}{\sqrt{hv - 285}}$$
(6)

where $N_{Z,n2}$ is the integrated intensity of the photoelectron peak associated with subshell n2 of element Z, hv is the x-ray energy, and E_8 is the binding energy of the atomic orbital which has been taken from an experimental collation of Siegbahn [8].

The photoelectron cross sections used in Eq. (6), $\sigma_{Z,n\lambda}$, have been calculated by Scofield [5]. His calculations are based on relativistic Hartree-Fock-Slater wave functions and have been carried out for each subshell of each atom. The values should be reliable so long as one is not too close to the threshold for photoionization, a condition which has been avoided in the use of Eq. (6). The calculated cross sections were checked by studying the relative intensities of photoelectric peaks observed in the gas phase of some simple molecules; and agreement between experiment and theory was found to be satisfactory.

Results of calculations for quantitative analysis

Using Eq. (6) we have calculated the relative intensities expected for photoelectron peaks for at least one subshell of every element from Z = 3to 92 for both Al Ka and Mg Ka x rays. For example, Fig. 2 gives the ratios for Al Ka radiation. The subshells chosen for calculations are those most likely to be used in ESCA. This frequently means that the subshells have the highest angular momentum for a given principal quantum number. This is so because vacancies in such orbitals cannot be filled by Coster-Kronig transitions, which can drastically shorten the half life of such states and thus broaden the photoelectron peak. To effect a quantitative analysis, the measured photoelectron intensities for different elements in a homogeneous sample need only be divided by ratios such as those given in Fig. 2.

In Table 1 are listed the relative intensities for elements in different solid compounds as determined from experimentally determined ratios of photoelectron intensities for known compounds, together with ratios calculated from Eq. (6). Although some scattering occurs amongst the different data, agreement between theory and experiment is quite satisfactory.

Chemical effects and inhomogeneity

The simple model as seen above would appear to give a reasonable basis

-5-



Fig. 2. Calculated intensities of photoelectron peaks from x-ray photoelectron spectra of solid. Results given are relative to the C(ls) peak for equal atomic concentrations. Calculations are for studies made with Al Ka x rays, hv = 1487 eV. Values are given for each element for different atomic subshells.

for quantitative analysis. In the future, improvements in both theory and experiment ought to be obtainable, but there are intrinsic difficulties which will prevent ultimate agreement of better than about 5%. For example, it has been noted that the intensities of photoelectron peaks of the same element separated by chemical shifts do not always follow the stoichiometric formula. This has sometimes been attributed to differences in the degree of electron shake up and shake off [9] for the different atoms of the molecule.

More important are the problems of inhomogeneity. Sometimes variation from expected behavior for a homogeneous material can be of help in characterizing the nature of the surface of a material. For example, if a homogeneous material containing two elements of known concentration lies below the surface of a contaminant layer the observed intensity will be

$$\frac{N_{1}}{N_{1}} = \frac{N_{1}^{\prime}}{N_{2}^{\prime}} e^{d(1/\lambda_{2}^{\prime} - 1/\lambda_{1}^{\prime})}$$
(7)

where N'_1/N'_2 is the ratio of intensities expected for a homogeneous

Table 1

Comparison of relative intensities for photoelectron peaks in solids $h\nu$ = Al $K\alpha$

	Experiment				Theoryd
<u>Ratio</u>	^I WAGNER ^a	ICARTER ^D	INEFEDOVC	Average	
C(ls)/F(ls)	0.24	0.29	0.24	0.25	0.277
C(ls)/Na(ls)	0.61	0.53	0.35	0.50	0.522
Na(ls)/F(ls)	2.09	1.44	1.89	1.80	1.32
Si(2p _{3/2})/F(1s.)	0.17	0.23	0.15	0.18	0.161
P(2p _{3/2})/Na(1s)	0.26	0.18	0.12	0.19	0.167
S(2p _{3/2})/Na(1s)	0.33	0.30	0.18	0.27	0.232
C1(2p _{3/2})/Na(1s)	0.46	0.43	0.25	0.38	0.312
K(2p _{3/2})/F(1s)	0.85	1.03	0.83	0.30	0.723
Ca(2p _{3/2})/F(1s)	1.01	1.06	0.98	1.02	0.903
Pb(4f _{7/2})/F(1s)	4.10	4.12		4.11	3.74
Na(2s)/Na(1s)	0.065	0.145	0.077	0.096	0.0919

^aRef. 1.

^bData from this report. Spectrometer coefficient has been corrected by dividing by the window width, E.

^CRef. 2.

^dCalculated from Eq. (6).

substance which can be obtained with the aid of Eq. (6). The mean-freepaths λ_1^{i} and λ_2^{i} are those for electrons of energy E_1^{i} and E_2^{i} in the contamination layer. If $1/\lambda_2^{i} - 1/\lambda_2^{i}$ is known or can be estimated, the thickness, d, of the contamination layer may be obtained. This method is suitable when the contamination layer is at least as thick as the smaller of the mean-free-paths. It is also desirable that the energy of the photoelectrons being observed differ as much as possible.

For the study of thinner layers it is advisable to measure elements in the contamination layer as well as the substrate. A fruitful area of research is the measurement of a metal and its oxide, since the chemical shift is often sufficient to easily identify the two species, and the photoelectron cross sections can be assumed to be identical. In this case the relative intensities of photoelectrons from the metal to those from the oxide should be for a uniform layer of contamination of thickness d

-7-

W.J. CARTER, G.K. SCHWEITZER, THOMAS A. CARLSON

$$\frac{N_{1}}{N_{2}} = \frac{n_{1}\lambda_{1}}{n_{2}\lambda_{2}'} \frac{e^{-d/\lambda_{2}'}}{(1-e^{-d/\lambda_{2}'})}$$
(8)

where λ_1 and λ_2 are respectively the mean-free-paths for electrons moving in the metal and in the oxide. For example, a tungsten-tungsten oxide system was studied [10] whereby the thickness of the oxide layer was varied by a series of anodization experiments. The thicknesses of the oxide layers were determined in separate experiments using radiochemical techniques. The experimental ratios of the photoelectron intensities were compared to the oxide thicknesses, and the plot which stretched over three orders of magnitude could be fitted to a single parameter. The excellence of the overall fit gave good evidence that the assumption of a uniform film of WO₃ was correct. This method of examining a two-component system by XPS can thus be used to ascertain the depth of the surface film (if λ_1 and λ_2 are known) and its uniformity.

CONCLUSIONS

A simple model has been developed with the help of photoelectron cross sections from Scofield to enable one to convert x-ray photoelectron spectroscopy of solids into a quantitative technique. This model can be used with effectiveness over the whole periodic table. Though accurate to only about 10% it means that the usefulness of x-ray photoelectron spectroscopy to surface analysis and chemical shifts can be supplemented with quantitative evaluation of the relative intensities of the elements present. The model is based on a homogeneous distribution of sample. Deviation from expectations may be used to evaluate the inhomogeneity of the surface layers.

REFERENCES

- 1 C.D. Wagner, Anal. Chem., 44(1972)1050.
- 2 V.I. Nefedov, N.P. Sergushin, I.M. Band and M.B. Trzhaskovskaya, J. Electron Spect., 2(1973)383.
- 3 C.A. Tolman, W.M. Riggs, W.J. Linn, C.M. King and R.C. Wendt, Inorg. Chem., 12(1973)2770.
- 4 J.H. Scofield, Lawrence Livermore Laboratory Report UCRL-51326 (1973). Specific values at hv = 1254 and 1487 eV were kindly supplied to us by the author.
- 5 S.T. Manson, J. Electron Spect., 1(1972/73)413.

A SIMPLE MODEL FOR QUANTITATIVE ANALYSIS

- 6 J.J. Quinn, Phys. Rev., 126(1962)1453.
- 7 From fit to compilations of experimentally determined mean-free-paths by J.C. Tracy (private communication) and C.J. Powell (to be published).
- 8 K. Siegbahn, <u>et al</u>., "ESCA", Nova Acta Regiae Soc. Sci. Upsaliensis ser. IV, 20(1967).
- 9 U. Gelius, in "Electron Spectroscopy", ed. by D.A. Shirley (North-Holland Publishing Co., Amsterdam, 1972) p. 311; D.P. Spears, thesis, University of Oklahoma (1974).
- 10 T.A. Carlson and G.E. McGuire, J. Electron Spect., 1(1972)161.