



Standard Guide for Identifying Chemical Effects and Matrix Effects in Auger Electron Spectroscopy¹

This standard is issued under the fixed designation E 984; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide outlines the types of chemical effects and matrix effects which are observed in Auger electron spectroscopy.

1.2 Guidelines are given for the reporting of chemical and matrix effects in Auger spectra.

1.3 Guidelines are given for utilizing Auger chemical effects for identification or characterization.

1.4 This guide is applicable to both electron excited and X-ray excited Auger electron spectroscopy.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

E 673 Terminology Relating to Surface Analysis²

E 827 Practice for Elemental Identification by Auger Electron Spectroscopy²

E 983 Guide for Minimizing Unwanted Electron Beam Effects In Auger Electron Spectroscopy²

E 996 Practice for Reporting Data in Auger Electron Spectroscopy²

3. Terminology

3.1 Terms used in Auger electron spectroscopy are defined in Terminology E 673.

4. Significance and Use

4.1 Auger electron spectroscopy is often capable of yielding information concerning the chemical and physical environment of atoms in the near-surface region of a solid as well as giving elemental and quantitative information. This information is manifested as changes in the observed Auger electron spectrum for a particular element in the specimen under study compared to the Auger spectrum produced by the same element when it

is in some reference form. The differences in the two spectra are said to be due to a “chemical effect” or a “matrix effect.” Despite sometimes making elemental identification and quantitative measurements more difficult, these effects in the Auger spectrum are considered valuable tools for characterizing the environment of the near-surface atoms in a solid.

5. Defining Auger Chemical Effects and Matrix Effects

5.1 In general, Auger chemical and matrix effects may result in (a) a shift in the energy of an Auger peak, (b) a change in the shape of an Auger electron energy distribution, (c) a change in the shape of the electron energy loss distribution associated with an Auger peak, or (d) a change in the Auger signal strengths of an Auger transition. The above changes may be due to the bonding or chemical environment of the element (chemical effect) or to the distribution of the element or compound within the specimen (matrix effect).

5.2 The Auger chemical shift is one of the most commonly observed chemical effects. A comparison can be made to the more familiar chemical shifts in XPS (X-ray photoelectron spectroscopy) photoelectron lines, where energy shifts are caused by changes in the ionic charge on an atom, the lattice potential at that atomic site, and the final-state relaxation energy contributed by adjacent atoms (**1 and 2**).³ Coverage by gas adsorbates on metal surfaces may also cause shifts in the metal Auger peak energies (**3**). The magnitude of the Auger chemical shift will usually be different from the XPS photoelectron shift because the Auger process involves a two-hole final state for the atom which is more strongly influenced by extra-atomic relaxation. Frequently an Auger chemical shift is larger than an XPS chemical shift (see Fig. 1).

5.2.1 Related to chemical shifts is the (modified) Auger parameter, defined as the sum of the photoelectron binding energy and the Auger electron kinetic energy (**4**). Because the Auger parameter is the difference between two line energies of the same element of the same specimen, it is independent of any electrical charging of the specimen and spectrometer energy reference level, making it easier to identify chemical states of elements in insulating specimens. Naturally, since both photoelectron lines and Auger lines must be measured, the Auger parameter can only be used with X-ray excited spectra.

¹ This guide is under the jurisdiction of ASTM Committee E-42 on Surface Analysis and is the direct responsibility of Subcommittee E42.03 on Auger Electron Spectroscopy and XPS.

Current edition approved Sept. 10, 1995. Published November 1995. Originally published as E 984 – 84. Last previous edition E 984 – 89.

² *Annual Book of ASTM Standards*, Vol 03.06.

³ The boldface numbers in parentheses refer to the references at the end of this standard.

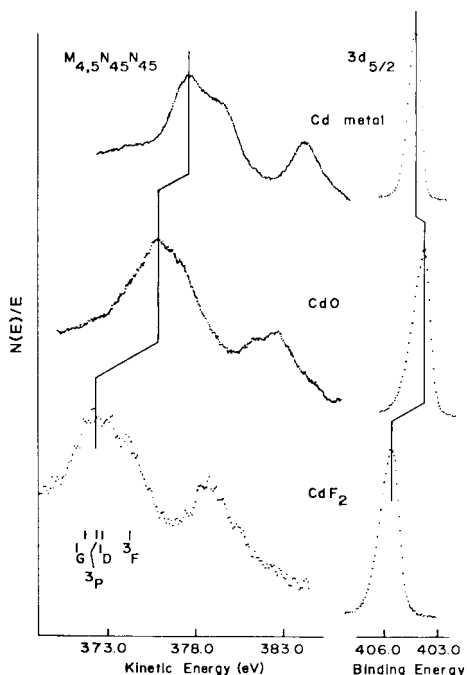


FIG. 1 Comparison of X-ray Excited Cd MNN Auger and 3d Photoelectron Energy Shifts for Cd Metal, CdO, and CdF₂(Ref 13)

5.3 The second category of chemical information from Auger spectroscopy is the Auger lineshapes observed for transitions involving valence electron orbitals. Shown in Fig. 2 and Fig. 3 are selected lineshapes for carbon KLL and aluminum LVV Auger transitions for different chemical states of those elements. While it is possible to relate the prominent

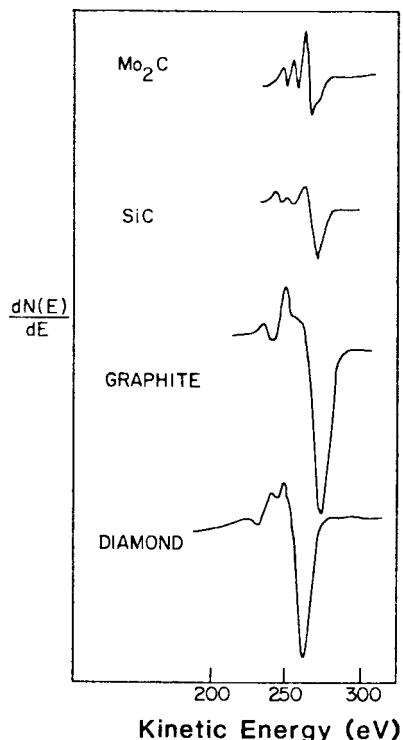
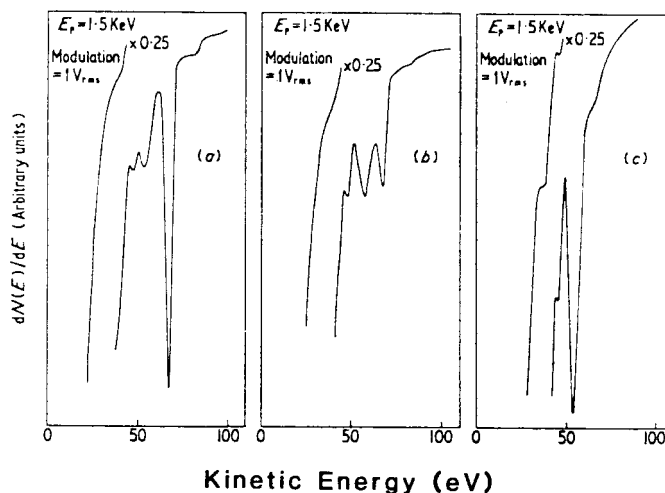


FIG. 2 Carbon KLL Auger Spectra for Mo₂C, SiC, Graphite, and Diamond (Ref 14)



(a) Almost no Oxidation (b) Partial Oxidation (c) After Oxidation has Reached a Saturation Stage

FIG. 3 Changes in the Aluminum LVV Auger spectrum as Oxygen is Absorbed on the Surface (Ref 15)

peaks in the Auger spectrum to transitions from particular bands in the density of states (for solids) or to particular molecular orbitals (for molecules) (5), this is not an easy task. The large number of possible two-hole final states, taken together with shake-up and shake-off transitions and uncertainty on all their final energies and intensities make the job of constructing a valence orbital density map from the Auger spectrum next to impossible for all but the simplest systems. Further, some spectra exhibit a quasiatomic character (6). Accordingly, most studies use the “fingerprint” approach when attempting to identify unknown species based on their Auger lineshape. Of course reference spectra are necessary in this approach for a positive identification.

5.4 Other effects besides energy shifts and valence lineshapes may be classified as chemical effects in Auger spectroscopy. For instance, many body effects in metals, such as plasmons, may make the lineshapes of Auger transitions of atoms in the metallic state very different from the Auger lineshapes for other chemical states, even for transitions involving only core-type electrons, Al and Mg (7). In single crystals, diffraction effects will produce different lineshapes (8). Relative intensities of several Auger transitions may change, either from attenuation of overlayers (9), or from different chemical states resulting in different Auger transition probabilities (10 and 11). Phonon broadening and inelastic electron energy loss effects will result in different linewidths and backgrounds for gases, adsorbates, and condensed phases (12).

6. Guidelines for Reporting Auger Chemical and Matrix Effects

6.1 In general, the guidelines outlined in Practice E 996 should be used. This practice covers reporting of the spectrometer, specimen preparation, excitation source, analyzer and detector modes, and data processing. Also, if measures were taken to control damage or charging of the specimen, report those conditions in a manner consistent with Guide E 983.

6.1.1 Practice E 827 should be used to confirm the elemental identification. The elemental information should be consistent with the presumed chemical state identification.

6.1.2 When reporting chemical and matrix effects in an Auger spectrum, the main feature of interest is the Auger peak energy (reported in eV). This is the energy of the largest negative excursion in the dN/dE spectrum or the most intense peak in the $N(E)$ spectrum. (Of course, these two peak positions' measurements will have different energy values.) The energy location of the major Auger peak should be in agreement with the reference value, consistent with the experimental parameters and calibrations as discussed in Practice E 996.

6.1.3 The reference level for the energy scale of the electron energy analyzer and the method for calibrating the energy scale should be specified. The relative peak energy shifts between the chemical states of interest and that element in its elemental state (or some other standard state) should also be reported.

6.1.4 Other spectral features which may be useful include the number, relative energy positions, and relative signal strengths of the secondary peaks. The reporting of these values should also be in agreement with the reference value and consistent with the experimental parameters and calibrations discussed in Practice E 996.

6.2 When spectra are presented for publication, the energy range should be wide enough that the shape of the background on either side of the Auger line is apparent. Shown in Fig. 4 are Auger spectra for several sulfur-containing compounds, and in Table 1 information from these spectra.

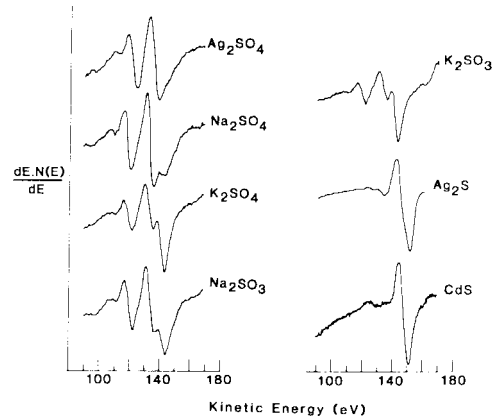


FIG. 4 Sulfur LVV Auger Spectra for Ag_2SO_4 , Na_2SO_4 , K_2SO_4 , Na_2SO_3 , K_2SO_3 , Ag_2S , CdS (Ref 16)

7. Keywords

7.1 Auger electron spectroscopy; chemical effect; matrix effect; spectroscopy

TABLE 1 Sulfur in Sulfur Compounds

NOTE 1—Data Compiled From Auger Spectra (Ref 16).

Compound	Electron Excited LVV ^{A,B}	New Peak ^A	$\Delta E^{A,C}$	X-ray Excited LVV ^{A,D}	Auger Parameter Plus Photon Energy ^{A,D}
K ₂ SO ₄	138.7	123.9	11.7
Ag ₂ SO ₄	141.7	127.4	8.7
Na ₂ SO ₄	138.3	123.0	12.1
Na ₂ SO ₃	139.1	124.8	11.3
K ₂ SO ₃	139.4	124.5	11.0
Ag ₂ S	150.4	149.3	516.9

^A Energy in eV.

^B Zero point of derivative spectra.

^C Ag₂S used for reference.

^D Al K α X rays.

REFERENCES

- (1) Wagner, C. D., and Biloen, P. "X-ray Excited Auger and Photoelectron Spectra of Partially Oxidized Magnesium Surfaces: The Observation of Abnormal Chemical Shifts," *Surface Science*, Vol 35, 1973, pp. 82–95.
- (2) Wagner, C. D., "Chemical Shifts of Auger Lines, and the Auger Parameter," *Discussions of the Faraday Society*, Vol 60, 1975, pp. 291–300.
- (3) Haas, T. W., and Grant, J. T., "Chemical Shifts in Auger Electron Spectroscopy from the Initial Oxidation of Ta(110)," *Physics Letters*, Vol 30A, 1969, p. 272.
- (4) Wagner, C. A., Gale, L. H., and Raymond, R. H., "Two-Dimensional Chemical State Plots: A Standardized Data Set for Use in Identifying Chemical States by X-ray Photoelectron Spectroscopy," *Analytical Chemistry*, Vol 51, 1979, pp. 466–482.
- (5) Jennison, D. R., "Understanding Core-Valence-Valence Auger Line-shapes," *Journal of Vacuum Science and Technology*, Vol 20, 1982, pp. 548–554.
- (6) Sawatsky, G. A., "Quasiatomic Auger Spectra in Narrow-Band Metals," *Physical Review Letters*, Vol 39, 1977, pp. 504–507.
- (7) Palmberg, P. W., "Quantitative Analysis of Solid Surfaces by Auger Electron Spectroscopy," *Analytical Chemistry*, Vol 45, 1973, pp. 549A–556A.
- (8) Chang, C. C., "Intensity Variations in Auger Spectra Caused by Diffraction," *Applied Physics Letters*, Vol 31, 1977, pp. 304–306.
- (9) Holloway, P. H., "Thickness Determination of Ultrathin Films by Auger Electron Spectroscopy," *Journal of Vacuum Science and Technology*, Vol 12, 1975, pp. 1418–1422.
- (10) Weissmann, R., "Intensity Ratios of the KL₁L₁, KL₂ L₂₃ Oxygen Auger Lines in Different Compounds," *Solid State Communications*, Vol 31, 1979, pp. 347–349.
- (11) Sarma, D. D., Hegde, M. S., and Rao, C. N. R., "An Auger Spectroscopic Study of the Surface Oxidation of Zinc," *Chemical Physics Letters*, Vol 73, 1980, pp. 443–446.
- (12) Houston, J. E. and Rye, R.R., "Chemical Analysis of Solid Surfaces," *Encyclopedia of Materials Science and Engineering*, Pergamon Press, Oxford, UK, Vol 1, 1986, pp 617–622.
- (13) Gaarenstroom, S. W., and Winograd, N., "Initial and Final State Effects in the ESCA Spectra of Cadmium and Silver Oxides," *Journal of Chemical Physics*, Vol 67, 1977, pp. 3500–3506.
- (14) Haas, T. W., Grant, J. T., and Dooley, III, G. J., "Chemical Effects in Auger Electron Spectroscopy," *Journal of Applied Physics*, Vol 43, 1972, pp. 1853–1860.
- (15) Suleman, M., and Pattinson, E. B., "Observation of a Plasmon-Gain in the Fine Structure of the Aluminum Auger Spectrum," *Journal of Physics, F: Metal Physics*, Vol 1, 1971, pp. L21–L24.
- (16) Turner, N. H., Murday, J. S., and Ramaker, D. E., "Quantitative Determination of Surface Composition of Sulfur Bearing Anion Mixtures by Auger Electron Spectroscopy," *Analytical Chemistry*, Vol 52, 1980, pp. 84–92.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).