



Designation: E984 – 06

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

This standard is issued under the fixed designation E984; 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:*²

E673 Terminology Relating to Surface Analysis (Withdrawn 2012)³

E827 Practice for Identifying Elements by the Peaks in Auger Electron Spectroscopy

E983 Guide for Minimizing Unwanted Electron Beam Effects in Auger Electron Spectroscopy

E996 Practice for Reporting Data in Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy

2.2 *Other Documents:*

ISO 18118:2004 Surface Chemical Analysis—Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy—Guide to the Use of Experimentally De-

termined Relative Sensitivity Factors for the Quantitative Analysis of Homogenous Materials

3. Terminology

3.1 Terms used in Auger electron spectroscopy are defined in Terminology **E673**.

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**).⁴ Coverage by

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ The boldface numbers in parentheses refer to the references at the end of this standard.

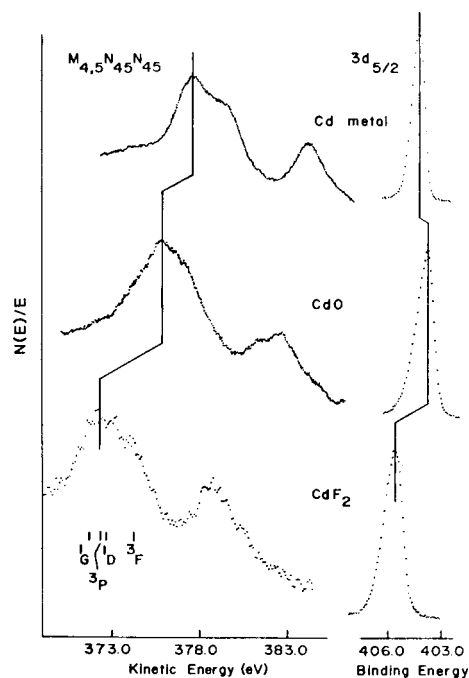


FIG. 1 Comparison of X-ray Excited Cd MNN Auger and 3d Photoelectron Energy Shifts for Cd Metal, CdO, and CdF₂ (Ref 13)

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.

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 electron-excited carbon KLL and aluminum LVV Auger transitions for different chemical states of those elements. While it is possible to relate the prominent 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

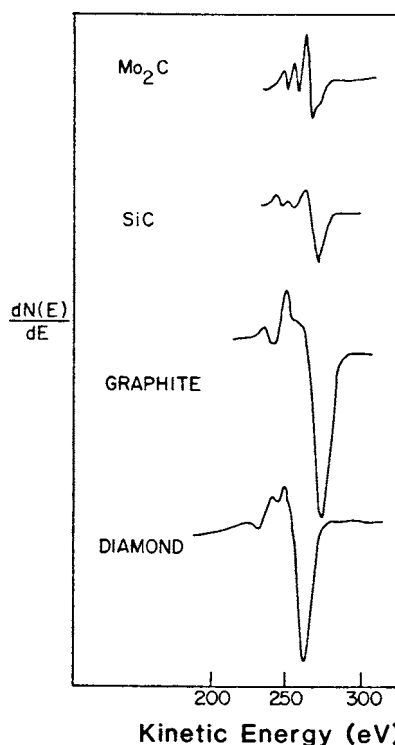
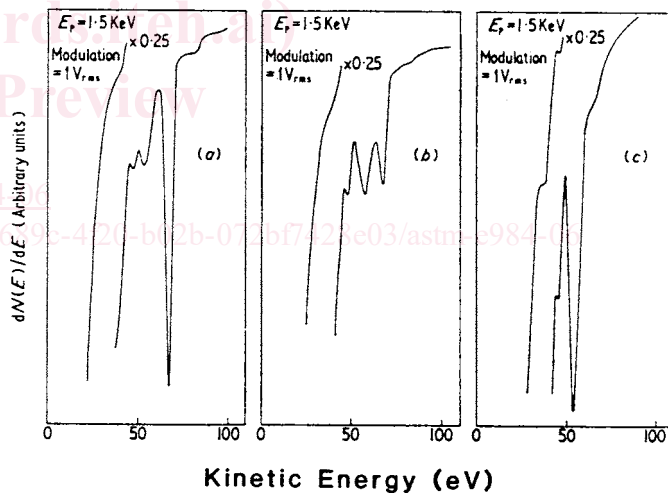


FIG. 2 Carbon KLL Auger Spectra for Mo₂C, SiC, Graphite, and Diamond (Ref 14)



(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)

when attempting to identify unknown species based on their Auger lineshape. Of course reference spectra are necessary in this approach for a positive identification. “Surface Science Spectra” is an international journal devoted to archiving surface science spectra of technological and scientific interest (17)