
Surface chemical analysis — Auger electron spectroscopy — Derivation of chemical information

*Analyse chimique des surfaces — Spectroscopie des électrons Auger
— Dédution de l'information chimique*

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Contents

Page

Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Abbreviated terms	1
5 Types of chemical and solid-state effects in Auger-electron spectra	1
6 Chemical effects arising from core-level Auger-electron transitions	3
6.1 General	3
6.2 Chemical shifts of Auger-electron energies	3
6.3 Chemical shifts of Auger parameters	4
6.4 Chemical-state plots	6
6.5 Databases of chemical shifts of Auger-electron energies and Auger parameters	7
6.6 Chemical effects on Auger-electron satellite structures	7
6.7 Chemical effects on the relative intensities and line shapes of CCC Auger-electron lines	8
6.8 Chemical effects on the inelastic region of CCC Auger-electron spectra	9
7 Chemical effects on Auger-electron transitions involving valence electrons	10
7.1 General	10
7.2 Chemical-state-dependent line shapes of CCV and CVV Auger-electron spectra	10
7.3 Information on local electronic structure from analysis of CCV and CVV Auger-electron line shapes	15
7.4 Novel techniques for obtaining information on chemical bonding from Auger processes	16
Bibliography	21

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: [Foreword — Supplementary information](#).

The committee responsible for this document is ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

This second edition cancels and replaces the first edition (ISO/TR 18394:2006), which has been technically revised.

Introduction

This Technical Report provides guidelines for the identification of chemical effects on X-ray or electron-excited Auger-electron spectra and for using these effects in chemical characterization.

Auger-electron spectra contain information on surface/interface elemental composition as well as on the environment local to the atom with the initial core hole^{[1][2][3][4][5]}. Changes in Auger-electron spectra due to alterations of the atomic environment are called chemical (or solid-state) effects. Recognition of chemical effects is very important in proper quantitative applications of Auger-electron spectroscopy and can be very helpful in identification of surface chemical species and of the chemical state of constituent atoms in surface or interface layers.

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Surface chemical analysis — Auger electron spectroscopy — Derivation of chemical information

1 Scope

This Technical Report provides guidelines for identifying chemical effects in X-ray or electron-excited Auger-electron spectra and for using these effects in chemical characterization.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115 (all parts), *Surface chemical analysis — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115 (all parts) apply.

4 Abbreviated terms

CCC	core-core-core (Auger-electron transition)
CCV	core-core-valence (Auger-electron transition)
CK	Coster-Kronig
c-BN	cubic boron nitride
CVV	core-valence-valence (Auger-electron transition)
DEAR-APECS	Dichroic Effect in Angle Resolved Auger-Photoelectron Coincidence Spectroscopy
h-BN	hexagonal boron nitride
IAE	Interatomic Auger Emission
ICD	Interatomic Coulomb Decay
PAES	Positron-Annihilation-induced Auger Electron Spectroscopy
REELS	Reflection Electron Energy-Loss Spectroscopy

5 Types of chemical and solid-state effects in Auger-electron spectra

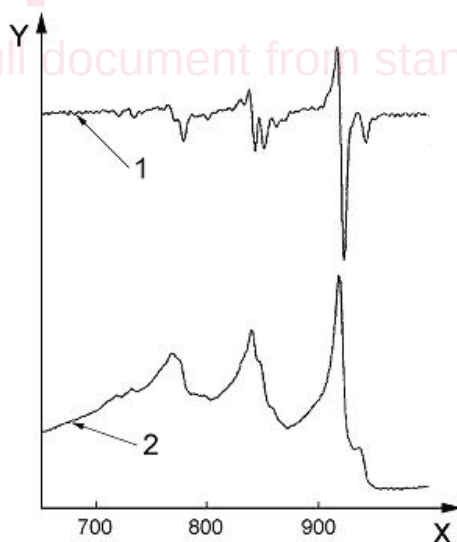
Many types of chemical or solid-state effects can be observed in Auger-electron spectra^{[1][2][3][4][5]}. Changes in the atomic environment of an atom ionized in its inner shell can result in a shift of the kinetic energy of the emitted Auger electron. In the case of X-ray-excited Auger-electron spectra, energy shifts of Auger parameters (i.e. kinetic-energy differences between Auger-electron peaks and the photoelectron peaks corresponding to the core levels involved in the Auger-electron process) can be detected as well. Furthermore, the line shape, the relative intensity and the satellite structure (induced by the intrinsic

excitation processes) of the Auger-electron lines can be considerably influenced by chemical effects, as can the structure of the energy-loss region (induced by extrinsic, electron-scattering processes) accompanying the intrinsic peaks. Strong chemical effects on the Auger-electron spectral shapes offer ways of identification of chemical species using the “fingerprint” approach.

In the case of electron-excited Auger-electron spectra, the Auger peaks are generally weak features superimposed on an intense background caused to a large extent by the primary electrons scattered inelastically within the solid sample. As a consequence, the differential Auger-electron spectrum is often recorded (or calculated from the measured spectrum) rather than the direct energy spectrum, facilitating the observation and identification of the Auger-electron peaks and the measurement of the respective Auger transition energies. Differentiation can, however, enhance the visibility of random fluctuations in recorded intensities, as shown in [Figure 1](#). If chemical-state information is needed from a direct energy spectrum, then the relative energy resolution of the electron spectrometer should be better than 0,15 % (e.g. 0,05 % or 0,02 %). A poorer energy resolution causes a significant broadening of the Auger-electron peaks and prevents observation of small changes of spectral line shapes or peak energies as chemical-state effects in the spectra. A great advantage of electron-excited Auger-electron spectroscopy over X-ray excitation with laboratory X-ray source, however, is the possibility of using high lateral resolution and obtaining chemical-state maps of surface nanostructures.

NOTE 1 Auger-electron spectra can be reported with the energy scale referenced either to the Fermi level or to the vacuum level. Kinetic energies with the latter reference are typically 4,5 eV less than those referenced to the Fermi level, but the difference in energies for these two references can vary from 4,0 eV to 5,0 eV since the position of the vacuum level depends on the condition of the spectrometer and may, in practice, vary with respect to the Fermi level. When energy shifts are determined from spectra recorded on different instruments, use of different energy references should be taken into account.

NOTE 2 While the visibility of noise features in a differential spectrum can be reduced by use of a larger number of channels in the calculation of the derivative, there may also be distortion of the resulting differential spectrum and loss of fine details associated with chemical-state effects.



Key

- X kinetic energy, eV
- Y intensity
- 1 differential spectrum
- 2 direct spectrum

NOTE This figure is reproduced from Figure 2.8 of Reference [1].

Figure 1 — Comparison of direct and differentiated Auger-electron spectra for copper (Cu LMM peaks)

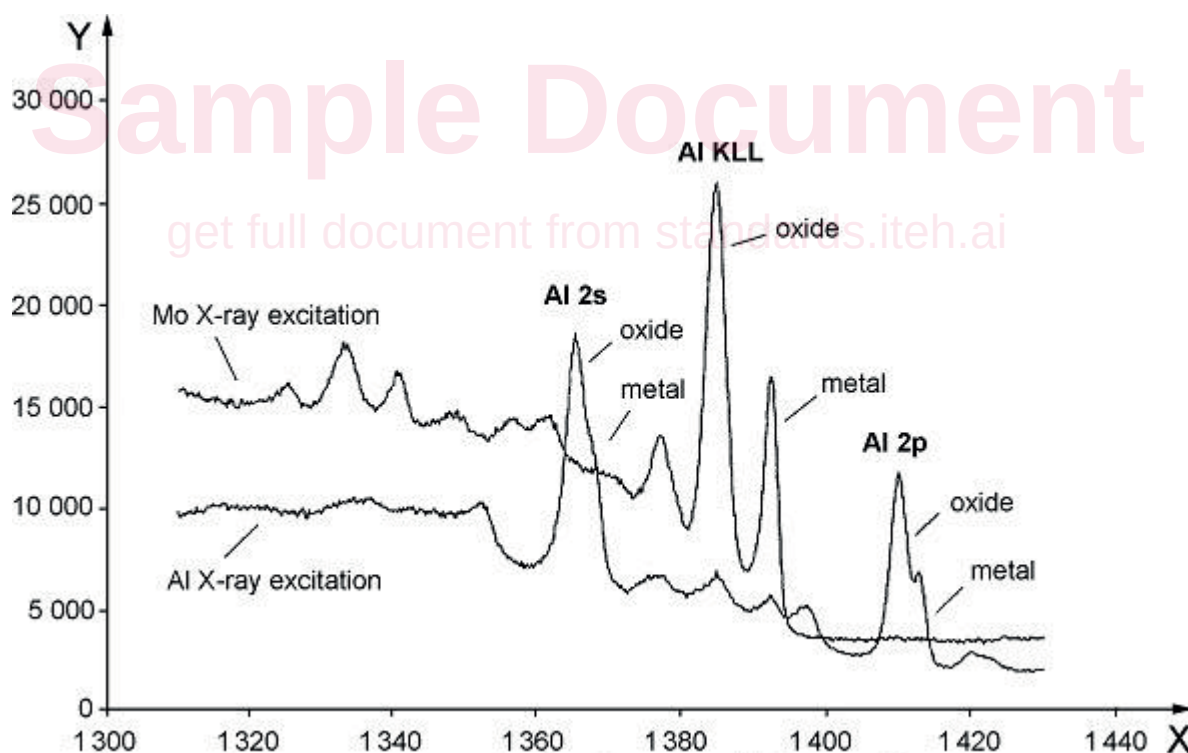
6 Chemical effects arising from core-level Auger-electron transitions

6.1 General

Core-level (or core-core-core, CCC) Auger-electron transitions occur when all of the levels involved in the Auger transition belong to the atomic core for the atom of interest.

6.2 Chemical shifts of Auger-electron energies

The main effect of any change in the solid-state environment on Auger-electron spectra for Auger transitions involving core levels is a shift of the Auger energies. This shift results from a change in the core atomic potential due to the changed environment and from a contribution due to the response of the local electronic structure to the appearance of core holes. Auger chemical shifts are generally larger than the binding-energy shifts of the atomic levels involved in the Auger-electron process because the two-hole final state of the process is more strongly influenced by relaxation effects. This phenomenon is illustrated by the example of aluminium and its oxide in Figure 2[6]. Large chemical shifts in the energy positions of the Auger-electron lines provide possibilities for chemical-state identification even in the case of electron-excited Auger-electron spectroscopy with, in this case, moderate energy resolution. In X-ray-excited Auger-electron spectra, the peak-to-background intensity ratios are usually larger than those in electron-excited spectra, facilitating accurate determination of peak energies. Recommended Auger electron energies are available for 42 elemental solids[7]. Information on Auger chemical shifts of particular elements can be obtained from handbooks[8][9][10][11] and online-accessible databases[12][13].



Key

- X kinetic energy, eV
Y intensity, counts/s

Figure 2 — Photoelectron and Auger-electron spectra of an aluminium foil covered by a thin overlayer of aluminium oxide: Excitation with Al and Mo X-rays