Present Status in Surface Analysis by Electron Spectroscopy

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Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) are the two techniques most commonly used for surface analysis. There are thousands of AES and XPS instruments in operation throughout the world, and these instruments have been successfully utilized to solve a great variety of scientific and technological problems. Because of this record of success and the fact that commercial instruments have been available for over 25 years, many scientists now rightly consider AES and XPS to be analytical techniques that can be used on a routine basis.

The conceptual basis for the main features observed in AES and XPS is relatively simple, and it is not usually difficult to make qualitative surface analyses by AES and XPS with the powerful capabilities of modern instruments. The energy scales of the instruments nevertheless do need to be adequately calibrated if measurements of binding energies or kinetic energies on different instruments are to be compared (e.g., for the determination of chemical shifts). Quantitative surface analyses by AES and XPS are generally much more difficult due to the influence of a large number of factors. These factors include scientific uncertainties about the physics of the AES and XPS processes, complexities in the experiments associated with the many modes of instrument operation, a large number of choices in selecting experimental paramotors, the need to ensure verification of instrument performance, artifacts in the acquired data, ambiguities in procedures, lack of needed reference data, and lack of adequate guidance [1]. The various difficulties can lead to frustration, inefficiency, and analyses with poor accuracy.

Reliable and efficient analyses by any technique require the availability of valid measurement methods based on adequate scientific understanding, reference procedures, reference data, reference materials, and laboratory intercomparisons using both the same technique and different techniques to give confidence that measurements of some known accuracy are being made. The growing adoption and use of ISO 9000 quality systems make it particularly important that adequate reference procedures be available for qualitative and quantitative surface analyses by AES and XPS.

I plan to give an overview of recent progress and remaining problems in surface analysis by AES and XPS. Most of the presentation will address factors important for quantitative

analysis. Table 1 gives a list of topics to illustrate, in this author's opinion, where there has been significant recent progress (generally within the past five years). There are, of course, other important topics [1] but they cannot be listed in the available space. References are given in Table 1 to papers that give summaries of recent results or that contain particularly useful information.

Some brief comments will now be given for the entries in Table 1. The UK National Physical Laboratory (NPL) has had a long-term program to develop calibration data and procedures for the energy and intensity scales of AES and XPS instruments [2-4]. Clibration procedures have been proposed and tested for AES [5] and XPS [6] energy scales. The XPS calibration procedure [6] has been utilized to perform retroactive calibrations of three instruments that have each been used to acquire binding-energy (BE) data for many elements. The corrected BE data and BE data from a fourth source have been compared, and mean elemental BE values have been computed with a standard deviation of 0.06eV [6].

Many workers [7-14] have shown that elastic-electron scattering can significantly modify the depth distribution function for signal electrons in AES and XPS; the angular distribution of signal electrons can also be appreciably modified in XPS. Simple models have been used for quantitative AES and XPS for many years in which elastic scattering has been ignored; it is then easy to show that the depth distribution function for the signal electrons is exponential. Inclusion of elastic-electron scattering makes the formalism more complex; guidance on the approach and inelastic-scattering data needed for different types of analyses is given in ref. 9.

A key problem in analyses by AES and XPS is the determination of the signal intensities. The approach of Tougaard [15, 16] is based on a reasonable physical model for transport of the signal electrons (unlike other empirical approaches).

The inelastic mean free path (IMFP) for the signal electrons in AES and XPS determines the surface sensitivity of the measurements and is required for quantitative analyses of homogeneous surfaces [9]. Tanuma et al. have calculated IMFP data for 27 elements and 29 compounds using an improved algorithm developed by Penn [17]. They have also developed a useful predictive formula, designated TPP-2M, for estimating IMFPs in other materials.

Table 1. Topics for which there has been significant progress in recent years.

- Calibration of instrumental energy and intensity scales [2-6]
- Improved knowledge of elastic-electron-scattering effects [7-14]
- Improved method for determining background due to inelastic scattering [15-16]
- Improved data for inelastic mean free paths [17]

- Improved correction algorithms for backscattering and topography in scanning AES [18-19]
- Growing availability of algorithms for data processing
- Growing availability of databases
  - X-Ray Photoelectron Spectroscopy Database [20-21]
  - Surface Science Spectra [20]
  - Common Data Processing System [22]
  - Elemental Auger-electron spectra [23]
- International cooperation in pre-standards research
  - VAMAS Technical Working Area 2 on Surface Chemical Analysis [24]
  - IUPAC Working Group on Surface Analysis [25]
- Growing number of reference procedures
  - ASTM Committee E-42 on Surface Analysis [26]
  - ISO Technical Committee 201 on Surface Chemical Analysis [27]

Table 2. Topics where additional development is needed.

- Matrix and Chemical Effects
  (a) Matrix Effects
  - Inhomogeneities/Morphology [1, 15]
  - Crystallinity [28-30]
  - Surface roughness [18, 19, 31]
  (b) Chemical Effects
  - Lineshapes in AES and XPS [32]
  (c) Matrix Factor in Quantitative AES and XPS
  - Corrections to elemental sensitivity factors [1]
- Inelastic Electron Scattering in the Vicinity of Surfaces and Interfaces (matrix effect)
  - Surface excitations [33, 34]
  - Inelastic mean free paths and effective attenuation lengths [9, 35]
- Complex Specimen Morphologies (matrix effect)
  - Monte Carlo simulations [7-14]
- Performance of Algorithms for Data Processing
  - Effects of operator choices on accuracy [16]

Improved algorithms have been developed by Prutton et al. [18] for the correction of backscattering and topography effects in scanning AES. Other powerful algorithms have been developed and applied for processing AES and XPS data (e.g., for pattern recognition, principal component analysis). More databases are becoming available for applications in AES and XPS

[20-23]. International cooperative projects in AES and XPS have been conducted under the Versailles Project for Advanced Materials and Standards (VAMAS) [24] and the International Union of Pure and Applied Chemistry [25]; these projects have ranged from laboratory intercomparisons to material characterizations, data formats, and terminology structure. Reference procedures for AES and XPS have been developed by ASTM Committee on E-42 on Surface Analysis [26] and are expected to be developed by the newly formed ISO Technical Committee 201 on Surface Chemical Analysis [27].

Table 2 is a listing of topics to indicate where further developments are needed. The magnitude of matrix and chemical effects is not well documented for many materials. Additional diagnostic techniques are required to identify the spatial extent of compositional nonuniformities [1, 15] and to describe the morphologies of different phases that may be present in certain types of specimens (e.g., bimetallic catalyst particles with an adlayer). The extent of crystalline order needs to be identified and its effect on measured intensities [28-30]. Further work needs to be done to correct for the effects of surface roughness on the observed intensities [18, 19, 31]. More documentation is needed of spectral lineshapes (particularly of so-called satellite features) in AES and XPS, and their changes with chemical state [32]. Procedures need to be developed for making specimen-specific corrections to elemental sensitivity factors for these matrix and chemical effects.

More data are needed to describe inelastic scattering processes and to determine IMFPs and effective attenuation lengths near surfaces and interfaces, particularly at low energies and for surfaces of varying roughness [33-35]. It may be necessary in the future to perform Monte Carlo simulations to obtain useful analyses on specimens with complex morphologies [7-10, 14]. Finally, performance attributes of the various algorithms used for data processing need to be better difined, particularly in regard to the effects of operator choices [16].

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