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Final Report from Group F: Reduction of Narrow Scan Data – Quantification

Participants: V. Fernandez, P. Graat, A. Jablonski, M. Jo, L. Kover, S. Maehl, C. J. Powell,
M. P. Seah, S. Tanuma, P. Weightman, L. Vanzetti
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1. Identification of Chemical State

(1) Assessment of compositional inhomogeneities in sample material

(a) Methods to identify possible lateral compositional inhomogeneities
- With use of imaging XPS
- Translating sample across analyzer field of view

(b) Methods to identify possible compositional inhomogeneities with depth
- Tilting sample to obtain XPS data for two widely separated emission angles (this approach is useful only if compositional inhomogeneities occur over depths up to the information depth for the measurements)
- Comparison of two peak intensities from the same element at widely separated energies (making use of the energy dependence of the electron inelastic mean free path)
- Removal of surface layers (e.g., by sputtering, chemical processes, etc.)
- Analysis of spectral lineshapes (e.g., with QUASES)

It would be helpful in the future for a user to know the information depths corresponding to the signals of interest (see section 3(5) below). With this information, the user could assess whether the sample is likely to be homogeneous or inhomogeneous over these depths.

(2) Estimation and assessment of trial sample composition

From measured peak intensities (see section 2(1) below), estimate composition for an identified phase.

Is this estimated composition close to that expected for the sample (e.g., if bulk composition is "known")?

What does this estimated composition imply for chemical shifts (of photoelectron lines, Auger lines, and Auger parameters). satellites, energy-loss features, and valence-band spectrum?

Is only one compound present?

- Compare measured spectra with reference spectra for known compounds where available (the reference spectra may have been measured previously on the same instrument or obtained from handbooks or databases).
- Compare measured spectrum with a calculated spectrum (if means to calculate spectra become conveniently available in the future).

(3) Consideration of possibility of multiple compounds in sample

Are multiple compounds expected or suspected?

- Examine chemical shifts for various possible stoichiometries.
- Examine presence of satellites.
- Compare measured spectrum with reference data for known compounds where available (or make measurements locally of suspected compounds).
- Consider whether measured spectrum is a linear combination of spectra for expected or suspected compounds (i.e., target factor analysis as described by W. F. Stickle and D. G. Watson, J. Vac. Sci. Tech. A **10**, 2806 (1992))), and determine percentages of each phase (although this approach will break down if there are different distributions of phases with position (e.g., depth)).
- Consider possible solutions or mixtures of components to produce either a single homogeneous phase (e.g., a polymer blend) or a mixture of phases. Is the measured spectrum a linear combination of spectra for separate phases? This test should be satisfactory unless there is the possibility of surface segregation or some other variation of composition with depth.

(4) Methods to identify chemical state

- (now) Consider peak positions, chemical shifts, lineshapes, energy-loss peaks, satellites, valence-band spectrum
- (now) Estimate rough composition from measured peak intensities
- (now) Compare measured spectrum with linear combinations of reference spectra for elements and compounds containing the detected elements using libraries of spectra or local measurements for the same measurement conditions (and modifications of the reference spectra where necessary to account for any difference of measurement conditions)
- (future) Compare measured spectrum with libraries of spectra using pattern recognition techniques (as proposed by Ahmad)
- Issues:
  1. Adequacy of spectral libraries now available (from Handbooks, *Surface Science Spectra*, Database of the Surface Analysis Society of Japan)
  2. How to modify reference spectra to account for local measurement conditions (e.g., by Simulation of Electron Spectra for Surface Analysis (SESSA) software, expected to be available in 2003)
  3. Availability of reference XPS spectra and intrinsic lineshapes for solid elements from NPL (expected to be available in 2003)

Comments:

Theoretical treatments of the electronic structure of metal alloys are not likely to be of much use in interpreting the spectral profiles of photoelectron and Auger-electron lines. Models such as the Anderson model of impurities in sp metals do not agree *in detail* with valence-band photoelectron spectra. More sophisticated theory (i.e., actually solving the Schroedinger equation) is only applicable to periodic structures. Studies of disordered alloys require further approximations (such as the coherent potential approximation). These approaches have had some limited success in calculating phase diagrams but are susceptible to local deviations from internuclear distances derived from Vegard's law.

Theoretical treatments of the electronic structure of materials are believed to be of limited value in the interpretation of photoelectron spectra. However, simple questions such as (a) Is the sample a metal? or (b) is the sample a transition metal? could be useful in helping to interpret photoelectron spectra. Metals have asymmetrical photoelectron lines (that can be represented by the Doniach-Sunjic lineshape as modified by the particular XPS measurement conditions). For transition metals, the asymmetry parameter in the Doniach-Sunjic lineshape expression can be large (up to 0.3) due to the presence of a large density of empty d states at the Fermi level. Finally, metals will not be susceptible to charging.

Nevertheless, Sherwood *et al*. (for example, A. A. Audi and P. M. A. Sherwood, Surf. Interface Anal. **33**, 274 (2002)) have successfully interpreted measured valence-band photoemission spectra of inorganic compounds with cluster and band-structure calculations. Similarly, calculations of valence-band spectra of ten polymers agreed well with experimental data; analysis of the partial densities of states led to assignments of spectral features to specific atomic groups of the polymer [S. Maehl, M. Neumann, B. Schneider, V. Schlett, and A. Baalmann, J. Polymer Science: Part A Polymer Chem, **37**, 95 (1999)]. In addition, Bureau *et al.* (see L. Kover, Surf. Interface Anal. **29**, 678-681 (2000)] have computed core-electron binding energies for about 200 molecules and some polymers with an accuracy (average absolute deviation) of about 0.2 eV in comparisons with experimental data.

(5) Methods to determine whether specimen is a conductor or a particular type of metal

(a) Is specimen a conductor?

A conductor will have valence-band states at its Fermi level. A measurement of the valence-band XPS spectrum can then be used to assess whether there are states (i.e., whether intensity is present) at zero binding energy (the Fermi level) within the combined energy resolution for the chosen measurement conditions and the possible drift of the binding-energy scale since the most recent calibration check. If intensity is present at the Fermi level as described, then the specimen is probably a conductor or a semiconductor; otherwise, it is a non-conductor or a material of low conductivity, and some precautions for charge control may be required. The qualification "probably" refers to the possibility that some intensity might be measured at zero binding energy for a non-conducting specimen if the surface was charging negatively at just the amount needed for the observation.

(b) Is specimen a "simple" metal or a transition metal?

The measured XPS valence-band spectrum for a conductor could also be compared with the convolution of the Fermi function and the resolution function of the instrument. If there was agreement in this comparison in the vicinity of zero binding energy, then the specimen is probably a "simple" sp-band metal rather than a d-band metal (such as a transition metal).

2. Quantification (composition, film thickness, spatial distribution of composition)

(1) Measurement of peak intensities

(a) Intensity measurement for a single peak (single chemical state of an element)

- For intensity measurements for a series of spectra for similar samples or for depth profiles where surface composition is not varying rapidly with depth, use of Shirley background to determine area of "main" peak is satisfactory (although absolute results will change depending on details of implementation).
- Use of a physical model for inelastic electron scattering to remove the inelastic-scattering background.
- It is also useful to apply the Tougaard algorithms [S. Tougaard, Surf. Science **162**, 875 (1985) and S. Tougaard, Surf. Science **244**, 125 (1991)] as quick checks of the sample homogeneity.

(b) Intensity measurements for overlapping peaks (multiple chemical states of an element or multiple elements)

- Peak-fits are required with curve-fitting software and use of analytic functions believed from experience to represent component lineshapes for measurement conditions.

Comment:
Yarzhemsky *et al.* [V. G. Yarzhemsky, V. I. Nefedov, M. B. Trzhaskovskaya, I. M. Band, and R. Szargan, J. Electron Spectrosc. Relat. Phenom. **123**, 1 (2002)] have reported calculations of "spectroscopic factors," the fraction of the total photoelectron intensity that goes in the main peak (i.e., the remaining intensity goes into shakeup or shakeoff). The computed spectroscopic factors for the 1s, 2p, 3d, and 4f photoelectron lines of many atoms range from 0.91 to 0.77. The authors also state that the "spectroscopic factors do not depend strongly on the chemical binding of any element under consideration in most cases." These results should be considered as a preliminary guide; validation of the atomic calculations is required. See also 4(6).

(2) Measurement of composition for an identified phase (homogeneous sample)

There are several approaches of varying accuracy:

(i) Use of relative sensitivity factors (for pure elements). The results will be approximate since no corrections have been made for different atomic densities or for matrix effects.

(ii) Use of average matrix relative sensitivity factors (see M. P. Seah, I. S. Gilmore, and S. J. Spencer, J. Electron Spectrosc. Relat. Phenom. **120**, 93 (2001) and ISO 18118 (in preparation)). See 4(1) below. This approach cannot be applied for electron energies less than about 150 eV.
Procedure:

(a) Measure elemental relative sensitivity factors for pure elements (e.g., as described in ISO 18118) or check values supplied with instrument.
(b) Compute average matrix relative sensitivity factors from the product of elemental relative sensitivity factors and the ratio of specified correction factors for that element and the corresponding correction factors for a hypothetical average matrix with specified material properties.

(iii) Direct comparison of spectra (e.g., for alloys) with standard spectra (if available).
(iv) "Multiline" approach of Ebel in which intensities for all observed lines are considered [see A. Jablonski, Pol. J. Chem. **74**, 1533 (2000)].

Recommendations:

- Use method (i), elemental relative sensitivity factors, as a simple means to obtain approximate composition.
- Use method (ii), average matrix relative sensitivity factors, to obtain more accurate composition.
- Use method (iii) if spectra for standards are available.
- Method (iv) is another option, but less documentation is available.

(3) Measurement of composition as a function of depth

Several "non-destructive" approaches are useful (to the extent that XPS measurements on a particular specimen for a given time can be regarded as non-destructive):

- Peakshape analysis using model for near-surface morphology and a model to correct for inelastic scattering [see, e.g., S. Tougaard, Surf. Interface Anal. **26**, 249 (1998) and W. S. M. Werner, L. Kover, J. Toth, and D. Varga, J. Electron Spectrosc. Relat. Phenom. **122**, 103 (2002)].
- Angle-resolved XPS. Many algorithms are available (e.g., Cumpson’s ARCtick software from NPL website) for analysis of data. See Cumpson review for details [P. J. Cumpson, J. Electron Spectrosc. Relat. Phenom. **73**, 25 (1995)].
- Diagnostics: measurements for two lines from the same element at widely separated energies; measurements for two different X-ray energies in some cases (where the resulting change in photoelectron energies gives significantly different attenuation lengths).

Comment:
See section 4(5) below for discussion of film-thickness measurements on non-flat surfaces.

Composition-versus-depth information can also be obtained "destructively" (e.g., by removal of surface "layers" by ion sputtering, chemical treatments, or mechanically). An existing ASTM standard (ASTM E 1078-97, Standard Guide for Specimen Preparation and Mounting in Surface Analysis) gives guidance on the use of ion sputtering, chemical etches, and mechanical methods such as angle lapping and ball-cratering; similar information is included in a draft ISO standard.

Comment:
See section 3(8) below for discussion of depth profiling by ion sputtering.

(4) Measurement of overlayer-film thickness

Several approaches are useful:

- Analysis of relative intensities for a substrate and an overlayer peak at a single emission angle.
- Analysis of relative intensities for a substrate and an overlayer peak at multiple emission angles. For data obtained at emission angles between 0^o and 60^o (with respect to the surface normal), a single value for the electron effective attenuation length can be used; see section 3(4) below for needed data. For larger emission angles, the effective attenuation length is a strong function of the emission angle.
- Use of "correction-factor" (CF) function for depth distribution function; see A. Jablonski and S. Tougaard, Surf. Interface Anal. **26**, 374 (1998).
- Peakshape analysis using model for near-surface morphology and a model to correct for inelastic scattering [see, e.g., S. Tougaard, J. Electron Spectrosc. **52**, 243 (1990) and W. S. M. Werner, L. Kover, J. Toth, and D. Varga, J. Electron Spectrosc. Relat. Phenom. **122**, 103 (2002)].
- It may also be possible to derive film thicknesses from analysis of intensities for two lines from the same element with widely different energies or from analysis of intensities of a line for two different X-ray energies (if the resulting photoelectron energies are sufficiently different). In both cases, use is made of the dependence of the inelastic mean free path on electron energy.

(5) Measurement of composition as a function of lateral position on the sample

Applications include determinations of elemental composition as a function of lateral position on the sample and determinations of variations of chemical state for an element as a function of position on the sample surface.

- Use of simple if approximate measure of peak intensity is often necessary in order to minimize spectral energy range and the data-acquisition time.
- Peakshape analysis is possible if spectral data can be acquired over a sufficient energy range using a model for near-surface morphology and a model to correct for inelastic scattering; see 2(3) above.
- Curve-fitting and background subtraction may be needed to determine intensities of overlapping components (e.g., for different chemical states of an element).
- Methods exist for intensity classification, analysis, and visualization (e.g., use of multivariate image analysis such as principal component analysis and diagrams); see K. Artyushkova and J. E. Fulghum, Surf. Interface Anal. **33**, 185 (2002).

Comment:
The analysis area (i.e., the sample area contributing all or a defined percentage of the photoelectron intensity) should be known for the chosen operating conditions and for compositional measurements of "small" features (features with dimensions up to ten times the lateral resolution of the instrument; see D. R. Baer and M. H. Engelhard, Surf. Interface Anal. **29**, 766 (2000).

3. Data Sources and Issues in Estimation of Uncertainties

The Guide to the Expression of Uncertainty in Measurement (GUM), a joint publication of the International Organization for Standardization (ISO), the Electrotechnical Commission, the International Organization of Legal Metrology, and the International Bureau of Weights and Measures in 1992, gives detailed recommendations for the expression and estimation of measurement uncertainties.

The following text is quoted from the Introduction to GUM:

"1. The uncertainty in the result of a measurement generally consists of several components which may be grouped into two categories according to the way in which their numerical value is estimated:

A. those which are evaluated by applying statistical methods to a series of repeated determinations,
B. those which are evaluated by other means.

"There is not always a simple correspondence between the classification into categories A or B and the previously used classification into "random" and "systematic" uncertainties. The term "systematic uncertainty" can be misleading and should be avoided.

"Any detailed report of the uncertainty should consist of a complete list of the components, specifying for each the method used to obtain its numerical value.

"2. The components in category A are characterized by the estimated variances, s_i^2, (or the estimated standard deviations s_i) and the number of degrees of freedom, ν_i. Where appropriate, the covariances should be given.

"3. The components in category B should be characterized by quantities u_j^2, which may be considered as approximations to the corresponding variances, the existence of which is assumed. The quantities u_j^2 may be treated like variances and the quantities u_j like standard deviations.

"4. The combined uncertainty should be characterized by the numerical value obtained by applying the usual method for the combination of variances. The combined uncertainty and its components should be expressed in the form of "standard deviations."

"5. If, for particular applications, it is necessary to multiple the combined uncertainty by a factor to obtain an overall uncertainty, the multiplying factor used must always be stated."

In Section 3.3.6 of GUM, it is stated that "the total uncertainty of the result of a measurement, termed *combined standard uncertainty* and denoted by u_c, is an estimated standard deviation equal to the positive square root of the total variance obtained by summing all variance and covariance (C.3.4) components, however evaluated, using the law of propagation of uncertainty."

In section 3.3.7 of GUM, it is stated that "an *expanded uncertainty U*, whose purpose is to provide an interval about the result of a measurement within which the values that could reasonably be attributed to the measurand may be expected to lie with a high level of confidence, is obtained by multiplying the combined standard uncertainty u_c by a *coverage factor k*. The choice of the factor *k*, which is usually in the range 2 to 3, is based on the level of confidence desired. Note – The coverage factor *k* is always to be stated so that the standard uncertainty of the measured quantity can be recovered for use in calculating the combined standard uncertainty of other measurement results that may depend on that quantity."

In section 6.3.3 of GUM, it is stated that "a reasonably adequate general approach to choosing a value of the coverage factor k and stating the level of confidence to be associated with the interval $Y = y \pm U = y \pm ku_c(y)$, is to recognize that the distribution of $(y - Y)/u_c(y)$ is approximately normal and to take $k = 2$ to obtain an interval having a level of confidence of approximately 95 percent, or to take $k = 3$ to obtain an interval having a level of confidence of approximately 99 percent."

(1) Uncertainty in peak energies

Uncertainties in derived binding energies may arise from:

(a) Measurements made after calibration of the binding-energy scale (ISO 15472)
(b) Statistics associated with peak fitting
(c) Charging

Notes: (i) Calibration parameters generally depend on instrumental settings (such as pass energy, aperture sizes, X-ray source).
(ii) Calibration should be checked soon after any instrumental change (e.g., bakeout).

Recommendation to XPS manufacturers and software developers: Uncertainties (a) and (b) above should be provided to the user.

(2) Uncertainties in peak intensities

Instrumental intensity scale may change with time due to:

- changes in detector efficiency (both absolute value and energy dependence)
- changes of instrumental settings and alignment (e.g., aperture settings)

Calibration software can be purchased from NPL.

ISO draft document "XPS - Repeatability and Constancy of Intensity Scale" is under consideration.

The signal linearity in XPS counting systems, the effective deadtime of pulse-counting systems, and the signal-to-noise ratio of XPS instruments have been discussed in recent papers [M. P. Seah and P. J. Cumpson, J. Electron Spectrosc. Relat. Phenom. **61**, 291 (1993); M. P. Seah, Surf. Interface Anal. **23**, 729 (1995); M. P. Seah, I. S. Gilmore, and S. J. Spencer, J. Electron Spectrosc. Relat. Phenom. **104**, 73 (1999)].

Detectors that provide an analog signal (e.g., CCD detectors) may have non-Poissonian statistics; for example, CCD detectors have read-out noise and background noise). XPS manufacturers should provide a conversion factor to give intensities in counts from CCD detectors as well as procedures to obtain the correct uncertainty of that intensity.

Software should provide estimates of uncertainties of peak intensities derived from curve fits.

Intensity uncertainty depends on how intensity values are used (e.g., if user is interested in absolute values or relative values).

(3) Inelastic mean free path (IMFP)

The IMFP is a useful parameter for describing effects of inelastic electron scattering in a material.

(a) Sources of IMFP Data

Calculations from experimental optical data for a "bulk" material (for materials where optical data over a sufficient photon energy range are available).

Measurements of elastic backscattering coefficients and analysis with a model for the elastic backscattering; software for deriving IMFPs from such measurements has been developed by A. Jablonski.

The predictive formula TPP-2M developed by Tanuma et al. [S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **21**, 165 (1994)] for electron energies between 50 eV and 2,000 eV. Use of this formula requires knowledge or estimates of the sample stoichiometry, the sample density, the number of valence electrons per molecule, and the bandgap energy (for a non-conductor).

The predictive formula G-1 developed by Gries [W. H. Gries, Surf. Interface Anal. **24**, 38 (1996)] for electron energies between 200 eV and 2,000 eV. Use of this formula requires knowledge or estimates of the sample stoichiometry and the sample density. This formula is believed to be more approximate than the TPP-2M formula [S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **25**, 25 (1997)].

The NIST Electron Inelastic-Mean-Free-Path Database is a useful source of IMFP data. This database provides:

- calculated IMFPs from experimental optical data for a "bulk" material, for materials for which sufficient optical data have been published
- IMFPs derived from experimental measurements of elastic backscattering coefficients and a model for elastic backscattering (the Elastic Peak Electron Spectroscopy (EPES) method), for materials where such IMFPs have been published
- IMFPs derived from the predictive IMFP formula TPP-2M, for bulk solids
- IMFPs derived from the more approximate predictive IMFP Gries formula G-1, for bulk

solids. This formula is useful because the stoichiometry and density are the only material parameter values required.

Notes

(i) If there is uncertainty in knowledge of needed parameters for use of the TPP-2M formula (density, number of valence electrons/molecule, bandgap energy), IMFPs should be determined for a reasonable range of these parameters.

(ii) IMFP data for bulk materials can be used in XPS until there is more definitive information on effects of surface excitations and roughness. For practical surfaces that are "rough," surface corrections are expected to be small. For "smooth" surfaces (e.g., silicon wafers), surface corrections could be significant, particularly for electron energies less than about 500 eV and for more grazing emission angles.

(b) Uncertainties of IMFP Data

The above-mentioned sources of IMFP data have the following uncertainties [C. J. Powell and A. Jablonski, J. Phys. Chem. Ref. Data **28**, 19 (1999)]:

- for IMFPs calculated from optical data, there is an uncertainty of about 10% associated with inconsistencies of the optical data (one-standard-deviation uncertainty). There is an additional uncertainty of 4.4% associated with differences of IMFPs calculated from different algorithms for a group of seven elemental solids.
- IMFPs values from EPES experiments for the same material show an internal consistency of 13.2% (for the same group of seven elemental solids).
- Consistency of IMFPs calculated from optical data and of IMFP values from EPES experiments is 17.4% (for the same group of elemental solids).
- Consistency of IMFPs from TPP-2M with respect to IMFPs calculated from optical data is 10%.
- Overall uncertainty of IMFPs from TPP-2M formula is about 20.5%; see C. J. Powell and A. Jablonski, Surf. Interface Anal. **29**, 108 (2000) and Users' Guide to NIST Electron Inelastic-Mean-Free-Path Database, Version 1.1 (2000).

(4) Effective attenuation length (EAL)

EAL values are needed for determination of overlayer-film thicknesses

Most measurements of EALs have been made from measurements of changes in substrate and overlayer AES or XPS intensities as an overlayer film of known thickness was deposited on a substrate. These EAL values generally have large uncertainties (arising from unknown sample morphologies, inaccurate measures of the overlayer thickness, and neglect of elastic-scattering effects); see C. J. Powell and A. Jablonski, J. Phys. Chem. Ref. Data **28**, 19 (1999).

EAL values can be obtained from:

- NIST Electron Effective-Attenuation Length Database, in which EALs are computed from an analytic expression derived from solution of the Boltzmann equation within the transport approximation; see C. J. Powell and A. Jablonski, Surf. Interface Anal. **33**, 211 (2002) and A. Jablonski and C. J. Powell, Surf. Science Reports **47**, 33

(2002). Comparisons of "practical" EALs from this approach with corresponding values obtained from Monte Carlo simulations (involving differential elastic-scattering cross sections obtained from relativistic Thomas-Fermi-Dirac atomic potentials) show mean percentage deviations of about 5% (for emission angles between 0^o and 80^o and for Si, Cu, and Au photoelectron and Auger-electron lines); see A. Jablonski and C. J. Powell (to be published).

- Predictive EAL formula of Seah and Gilmore [M. P. Seah and I. S. Gilmore, Surf. Interface Anal. **31**, 835 (2001)]. This predictive formula (for the ratio of the EAL to the corresponding IMFP) agrees with the results of Monte Carlo simulations (involving differential elastic-scattering cross sections obtained from relativistic Hartree-Fock-Slater atomic potentials) with a standard deviation of 1.2% for an emission angle of 45^o.

(5) Information depth (ID) and mean escape depth (MED)

The ID is the maximum depth, normal to the surface, from which all or a defined percentage of the signal of interest originates (ISO 18115); for example, this percentage could be 90%, 95% or 99%.

The ID for a particular material, photoelectron energy, and measurement conditions is helpful in assessments of whether the sample is homogeneous over that depth.

The MED is a useful measure of surface sensitivity. The MED is the average depth normal to the surface from which the photoelectrons escape, as defined by $\int_0^\infty z\phi(z,\alpha)dz / \int_0^\infty \phi(z,\alpha)dz$ where $\phi(z,\alpha)$ is the emission depth distribution function for depth z from the surface into the material and for angle of emission α with respect to the surface normal (ISO 18115).

Ratios of the ID and the MED to the corresponding simple values computed with neglect of elastic-electron scattering are qualitatively similar to related ratios of the EAL to the IMFP. Elastic scattering generally needs to be considered in determinations of the ID and the MED; see A. Jablonski and C. J. Powell (to be published).

Sources of MED data:

- NIST Electron Effective-Attenuation-Length Database
- Predictive MED formula; see A. Jablonski, I. S. Tilinin, and C. J. Powell, Phys. Rev. B **54**, 10927 (1996).

Notes:

1. The formal definitions of the ID and MED are limited to homogeneous materials but can be extended to samples with compositions varying with depth.
2. Evaluations of the ID and MED for samples having concentration gradients with depth could be made if the inelastic mean free path and transport mean free path (for the photoelectron signal) do not vary significantly with depth.

3. MEDs computed from transport theory differ from corresponding values obtained from Monte Carlo simulations by up to 3%; see A. Jablonski, I. S. Tilinin, and C. J. Powell, Phys. Rev. B **54**, 10927 (1996) and A. Jablonski and C. J. Powell (to be published).

(6) Corrections for effects of elastic scattering on surface composition

Two parameters provide useful corrections for effects of elastic scattering on determinations of surface composition:

- Q_x is a factor describing reduction of photoelectron intensity ($Q_x < 1$).
- β_{eff} is the effective photoionization asymmetry parameter.

Sources of Q_x and β_{eff} data:

- Tabulations [A. Jablonski, Surf. Interface Anal. **23**, 29 (1995)]
- NIST Electron Effective-Attenuation Length Database
- Seah and Gilmore predictive formula [M. P. Seah and I. S. Gilmore, Surf. Interface Anal. **31**, 835 (2001)]

Both corrections (Q_x and β_{eff}) should be used in equations to give surface composition (for a homogeneous sample).

Notes:

1. Differential elastic-scattering cross sections are needed for "advanced" corrections of elastic-scattering effects in XPS (e.g., for Monte Carlo simulations of photoelectron transport).
2. Differential elastic-scattering cross sections are available from the NIST Electron Elastic-Scattering Cross-Section Database, SRD 64, Version 2.0 (2000).
3. The differential cross sections in SRD 64 have been computed for free atoms. These data have been found useful for investigations of photoelectron transport in solids where "large-angle" elastic scattering is significant; see A. Jablonski and C. J. Powell, Surf. Science **463**, 29 (2000).

(7) Uncertainties in use of tables of elemental relative sensitivity factors and in use of average matrix relative sensitivity factors

Tables of elemental relative sensitivity factors (RSFs) are often provided in the software of XPS instruments for specified measurement conditions. Analyses with these RSFs have uncertainties associated with the neglect of matrix corrections.

The application of elemental RSFs is limited to instruments that have had their intensity scale calibrated or to instruments that are constant in behaviour.

The table of elemental RSFs can be adjusted by the user for local measurement conditions using the procedure described in ISO 18118.

Average matrix RSFs (see 4(1)) provide more reliable analyses since matrix corrections (necessary when using elemental RSFs) are then minimized.

Average matrix RSFs work well for all subshells except for s subshells above 1s.

(8) Other factors

(a) Depth Profiling

A number of physical factors can influence the reliability of composition-versus-depth information derived from composition measurements obtained as a specimen is bombarded by an ion beam. Ideally, "layers" of the material would be removed at a uniform and known rate so that a physically meaningful depth profile but a number of complicating factors can arise. These factors include preferential sputtering, ion-induced mixing, chemical reduction, ion-stimulated diffusion and segregation, charging (and differential charging), generation of defects, and changes of surface topography (ranging from increased average roughness to the generation of etch pits, pyramids, cones, whiskers and corrugation on specific types of materials). Brief information on these factors is given in an ASTM standard (ASTM E 1078-97, Standard Guide for Specimen Preparation and Mounting in Surface Analysis) and a related draft ISO standard. More detailed information is given in a book chapter [L. S. Dake, D. E. King, J. R. Pitts, and A. W. Czanderna, in *Beam Effects, Surface Topography, and Depth Profiling in Surface Analysis*, Plenum, New York, 1998, pp.97-274].

Preferential sputtering, ion-induced mixing, chemical reduction, and ion-stimulated diffusion and segregation all change the composition to be measured. For example, the amount of anion species in a compound may be reduced by up to a factor of two. These effects can be minimized by working with photoelectrons of the highest possible energy. The best solution is to make comparisons with data for reference materials wherever possible.

(b) Electron-diffraction of forward-focusing effects.

These effects can lead to enhanced intensities along low-index directions when measurements are made on a crystalline material (e.g., a single grain of a polycrystalline material). Intensity enhancements of up to about 50% are possible. See S. A. Chambers, Surf. Science Reports **16**, 261 (1992).

Angular scans can be made to test for the existence of these effects.

Effects can be minimized by:

- maximizing acceptance angle of analyzer
- sputtering sample to reduce crystallinity
- sample rotation

(c) Analysis area

An ISO standard to measure analysis area is under development. The analysis area is generally some multiple (of up to about 10) of the area calculated from the lateral resolution considered as a radius; see D. R. Baer and M. H. Engelhard, Surf. Interface Anal. **29**, 766 (2000). The analysis area can vary with photoelectron energy.

(d) Specimen degradation

The surface composition of certain types of materials can change under X-ray irradiation during XPS measurements. Since the rate of specimen degradation will increase with X-ray flux density and measurement time, there will be a limit to the measurement time (before which "negligible" changes in surface composition occur) for particular measurement conditions and particular types of materials. Compromises will generally have to be made between spatial resolution, energy resolution, and sensitivity for the detection of particular photoelectron signals and the amount of specimen degradation that is acceptable. A recent book chapter [J. H. Thomas, in *Beam Effects, Surface Topography, and Depth Profiling in Surface Analysis*, Plenum, New York, 1998, pp.1-37] gives information on X-ray-induced degradation of polymers and some inorganic compounds. Yoshihara and Tanaka [Surf. Interface Anal. **33**, 252 (2002)] recently reported degradation rates for poly(vinyl chloride), nitrocellulose, and poly(tetrafluoroethylene) by X-rays in XPS.

(9) Uncertainty of Final Results

The final uncertainty of a result depends on the proper combination of estimates of random and systematic errors appropriate to the method used for obtaining the result. These uncertainties should be combined depending on the nature of the calculational algorithm (e.g., with use of absolute or relative uncertainties depending on whether parameters are being added/subtracted or multiplied/divided, respectively.

Useful comparisons can often be made of results having the needed precision (repeatability) rather than requiring results of high accuracy.

4. New/Improved Methodology and Data for XPS

(1) Use of average matrix relative sensitivity factors (AMRSFs)

The uncertainty in the determination of a surface composition will be less if AMRSFs are used than with the conventional elemental relative sensitivity factor approach because ratios of parameters are employed [see M. P. Seah, I. S. Gilmore, and S. J. Spencer, J. Electron Spectrosc. Relat. Phenom. **120**, 93 (2001) and ISO 18118 (in preparation)].

(2) Test for variations of composition as a function of depth (stratification)

Plot ratio of two wide-scan spectra recorded for two well-separated emission angles (e.g., 0^o and 75^o with respect to the surface normal). Variations in the plotted ratio with binding energy will indicate whether the sample composition varies with depth [see M. P. Seah, J. H. Qiu, P. J. Cumpson, and J. E. Castle, Surf. Interface Anal. **21**, 336 (1994). The same approach can be used to examine intensities of different chemical states of an element.

(3) Effects of surface roughness on measurements of overlayer thicknesses

Calculations and some limited experimental data indicate that the effects of surface roughness on overlayer-film thicknesses calculated from photoelectron intensities may be minimized if the intensity measurements are made at emission angles between 35^o and 55^o. See P. L. J. Gunter and J. W. Niemantsverdriet, Appl. Surf. Science **89**, 69 (1995); W. S. M. Werner, Surf. Interface Anal. **23**, 696 (1995); P. L. J. Gunter, O. L. J. Gijzeman, and J. W. Niemantsverdriet, Appl. Surf. Science **115**, 342 (1997); and P. Kappen, K. Reihs, C. Seidel, M. Voetz, and H. Fuchs, Surf. Science **465**, 40 (2000). See also work of C. S. Fadley [Prog. Solid State Chemistry 11, 265 (1976)] and M. F. Ebel and J. Wernisch [Surf. Interface Anal. 3, 191 (1981)].

The results of the calculations depend on specific models for the roughness.

The use of simple parameters such as the root-mean-square roughness is probably insufficient.

(4) Measurement of overlayer-film thicknesses

The "Thickogram" is a useful algorithm for the determination of overlayer-film thicknesses from the intensities of substrate and overlayer photoelectron intensities for lines with significantly separated energies [see P. J. Cumpson, Surf. Interface Anal. **29**, 403 (2000)].

The published nomogram was derived from an approximate expression for electron attenuation lengths (EALs) that is valid for electron energies above about 500 eV. This approach could be extended, if needed, to lower energies using available data for EALs.

(5) Determinations of overlayer-film thicknesses on non-planar substrates

Fulghum and Linton [J. E. Fulghum and R. W. Linton, Surf. Interface Anal. **13**, 186 (1988)] have reviewed methods of XPS quantitation and determination of overlayer-film thicknesses for films on non-planar substrates, such as powders or particles of high surface area. Mohai and Bertoti [M. Mohai and I. Bertoti (to be published)] have developed software for computing layer thicknesses on curved surfaces that are considered to be either spherical or cylindrical.

(6) Relative quantification of different chemical states for the same element

- The spectrum often consists of two or more peaks that may overlap by varying amounts.
- Software should provide estimates of uncertainties of intensities derived from curve fits.
- It is generally assumed that the fraction of photoelectron intensity due to shakeup does not depend on chemical state, but this assumption is known to be incorrect for carbon compounds and for Cu compounds (see also 2(1)). For discussion of varying shakeup intensities in the C 1s spectra of polymers, see G. Beamson and D. Briggs, High Resolution XPS: The Scienta ESCA300 Database (Wiley, Chichester, 1992), pp. 37-39. For discussion of shakeup satellites in Cu compounds, see J. E. Castle, Surf. Interface Anal. **33**, 196 (2002). The spectral lineshapes of shakeup satellite can

be different in Cr, Fe, and Fe compounds [J. E. Castle, same reference], but it is generally not easy to make reliable measurements of intensity ratios of shakeup peaks to the main peak.