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ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON MICROCHEMICAL TECHNIQUES AND TRACE ANALYSIS*

GENERAL ASPECTS OF TRACE ANALYTICAL METHODS—IV. RECOMMENDATIONS FOR NOMENCLATURE, STANDARD PROCEDURES AND REPORTING OF EXPERIMENTAL DATA FOR SURFACE ANALYSIS TECHNIQUES

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Comments from the viewpoint of languages other than English are especially encouraged. These may have special significance regarding the publication in various countries of translations of the nomenclature eventually approved by IUPAC.

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PROVISIONAL

RECOMMENDATIONS FOR NOMENCLATURE, STANDARD PROCEDURES AND REPORTING OF EXPERIMENTAL DATA FOR SURFACE ANALYSIS TECHNIQUES

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Abstract - Because of the rapid growth of modern physical techniques for the analysis of solid surfaces, a series of recommendations are provided to simplify the communication of results using these diverse methods. Standard technique names are presented and the general nomenclature for surface studies are clarified. Methods for the preparation of samples for surface analysis are provided and the specification of information to be included in the preparation of scientific publications is formulated.

INTRODUCTION

The most important problem faced by a scientist at the start and at the conclusion of an experiment is communicating with other scientists. Since the type and quantity of information reported in scientific papers varies widely in the field of "surface analysis", it is the aim of these recommendations to suggest standard preparation procedures and methods of data reporting, and to clarify nomenclature for these various techniques.

It is first necessary to recommend standard technique names, then to clarify nomenclature, before suggesting a cleaning method and finally specifying the information needed to be included in a scientific paper describing an experiment using one of these techniques. (see Note a)

TECHNIQUE NOMENCLATURE

Auger Electron Spectroscopy (AES). The technique in which a sample is bombarded with keV-energy electrons or X-rays in a high vacuum apparatus, and the energy distribution of the electrons produced through radiationless de-excitation of the atoms in the sample is recorded; the derivative curve may also be recorded.

UV Photoelectron Spectroscopy (UPS). Any technique in which the sample is irradiated by monochromatic radiation of the ultraviolet region and the energy distribtuion of the photoelectrons emitted by the sample is measured. The spectra originate from excitation of valence electrons and particularly lead to the identification of interatomic groupings within molecules and to the electronic structure of clean surfaces.

X-Ray Photoelectron Spectroscopy (XPS). Any technique in which the sample is bombarded with X-rays and photoelectrons produced by the sample are detected as a function of energy. ESCA (Electron Spectroscopy for Chemical Analysis) refers to the use of this technique to identify elements, their concentrations, and their chemical state within the sample.

Note a. The nomenclature given is provisional. Commission I.6 (COMMISSION ON COLLOID AND SURFACE CHEMISTRY) is engaged in the preparation of a manual of nomenclature in surface physics.

Rutherford Back Scattering (RBS) also referred to as Backscattering Spectrometry (BSS). Any technique using high energy particles directed toward a sample, in which the bombarding particles are detected and recorded as function of energy and/or angle. The technique is mostly used for determining depth distributions of elements based on the energy of the backscattered particle. In general, He^+ or H^+ particles are used at energies in the order of 100 keV to some MeV.

Ion Scattering Spectrometry (ISS). Any technique using low energy ($\lesssim$ 10 keV) ions in which the bombarding particles scattered by the sample are detected and recorded as a function of energy and/or angle. This technique is used mainly for determining the composition and structure of the first few atomic layers of a sample.

Secondary Ion Mass Spectrometry (SIMS). Any technique in which the sample is bombarded with a stream of (primary) ions and the (secondary) ions ejected from the sample are detected after passage through a mass spectrometer.

Ion Probe Microanalysis refers to the use of SIMS for qualitative and quantitative elemental analysis with a spatial resolution of less than 10 μm.

Ion Microscopy refers to the use of the SIMS technique to obtain micrographs of the elemental (or isotopic) distribution at the surface of a sample with a spatial resolution of 2 μm or better.

GENERAL NOMENCLATURE

In this section we attempt to define a number of terms used in the literature in connection with the above techniques.

Trace Element. Any element having an average concentration of less than about 100 parts per million atoms (ppma) or less than 100 μg per g.

Thin Film. A material which has been deposited or adhered to a substrate and has a uniform thickness within 20% of its average thickness, which is less than about 10 μm.

Interface. A boundary between two condensed phases. Experimentally, the portion of the sample through which the first derivative of any concentration vs. location plot has a measureable departure from zero. An interface between a solid phase and a gaseous phase is called a surface.

Surface. It is recommended that for the purpose of surface analysis a distinction be made between "surface" in general, "physical surface" and "experimental surface":

> Surface - The "outer portion" of a sample of undefined depth; to be used in general discussions of the outside regions of the sample.
>
> Physical Surface - That atomic layer of a sample which, if the sample were placed in a vacuum, is the layer "in contact with" the vacuum; the outermost atomic layer of a sample.
>
> Experimental Surface - That portion of the sample with which there is significant interaction with the particles or radiation used for excitation. It is the volume of sample required for analysis or the volume corresponding to the escape for the emitted radiation or particle, whichever is larger.

Concentration in Experimental Surface (often called Surface Concentration). The amount of the material of interest divided by the total amount of substances in the volume of interest. Concentration may be defined in terms of numbers of atoms (particles) (ppma) or in terms of weight (μg/g).

Monolayer. Coverage of a substrate by one atomic or molecular layer of a species. The term monolayer expresses that all elementary units of the adsortive atoms or molecules are in contact with the surface as opposed to the term MULTILAYER which designates that more than one layer of the adsorptive species covers the surface and not all units are in contact with the surface layer of the substrate (1).

Monolayer Capacity: For chemisorption the amount of adsorbate which is needed to occupy all adsorption sites as determined by the structure of the adsorbent and by the chemical nature of the adsorptive. For physiosorption the amount needed to cover the surface with a complete monolayer of atoms or molecules in close packed array, the kind of close packing having to be stated explicitly when necessary.

Surface Coverage. For both monolayer and multilayer coverage defined as the ratio of the amount of substances covering the surface to the monolayer capacity (1). Coverage is unity when one complete monolayer is deposited onto the sample.

Surface Contamination. Material in the experimental surface which is either not characteristic of the sample or which would not be present if the sample had been prepared in an absolute vacuum by methods not contacting other substances to the sample.

Clean Surface. An experimental surface having no surface contamination observable by means of the used method.

Matrix Effects (2). Effects which cause changes in Auger-Electron, photoelectron, secondary ion yield, or scattered ion itensity, the energy or shape of the signal of an element in any environment as compared to these quantities in a pure element.

(a) Chemical Matrix Effects: Changes in the chemical composition of the solid which affect the signals as described above.

(b) Physical Matrix Effects: Topographical and/or crystalline properties which affect the signal as described above.

Chemical Shift. The displacement of photoelectron or Auger peak energies originating from changes in electron binding energies as a consequence of differences in the chemical environment of the atoms.

Auger Electron Yield. The fraction of the atoms having a vacancy in an inner orbital which relax by emission of an Auger electron.

Photo Electron Yield. The number of photoelectrons emitted by the sample per incident photon.

Secondary Ion Yield. The number of secondary ions generated at the surface of the sample per primary ion.

Sputter Yield (2). The number of particles sputtered from the surface of a target per primary ion.

Escape Depth. After Thomas (3), the distance into the sample measured from the physical surface from which all but a fraction 1/e of the particles or radiation detected have originated.

Depth Profile. Dependance of concentration on depth perpendicular to the surface in a solid sample. It can be obtained by a simultaneous or sequential process of erosion and surface analysis or by measurement of the energy loss of primary backscattered or particles produced by nuclear reactions.

Depth Resolution. The distance between the 84 and 16 percent level of the depth profile of an element in a perfect sandwich sample with an infinitesimally small overlap of the components (4). These limits corresponds to the 2σ-value of the Gaussian distribution of the Gaussian distribution of the signal at the interface (Fig. 1).

Sputtering. Removal of surface material (atoms, clusters and molecules) by particle bombardment.

Absolute Detection Limit. Smallest detectable amount of an element or compound (3σ-criterion) on or in a particular sample - given in mass units or absolute number of atoms or molecules.

Relative Detection Limit (often incorrectly referred to as sensitivity). Smallest amount of material detectable (3σ-criterion) in a matrix relative to the amount of material analysed - given in atomic, mole or weight fractions.

Qualitative Elemental Specificity. Ability of a method to detect one element in the presence of another element.

PREPARATION OF SAMPLES FOR ELEMENTAL ANALYSIS OF SURFACES

Following whatever polishing may be deemed appropriate for the sample and method of analysis to be used, the following sample cleaning sequence (5) is suggested unless the desired analysis precludes or prevents the use of one or more steps; ultrasonic washing in each of the following solvents sequentially - trichlorethylene, acetone, deionized water, hot deionized water - at least one minute per wash. Heating in vacuum (preferable within the chamber in which the analysis is to be done to prevent contamination during transfer) to 150°C, with the vacuum conditions at least as good as the vacuum conditions to exist during the experiment.

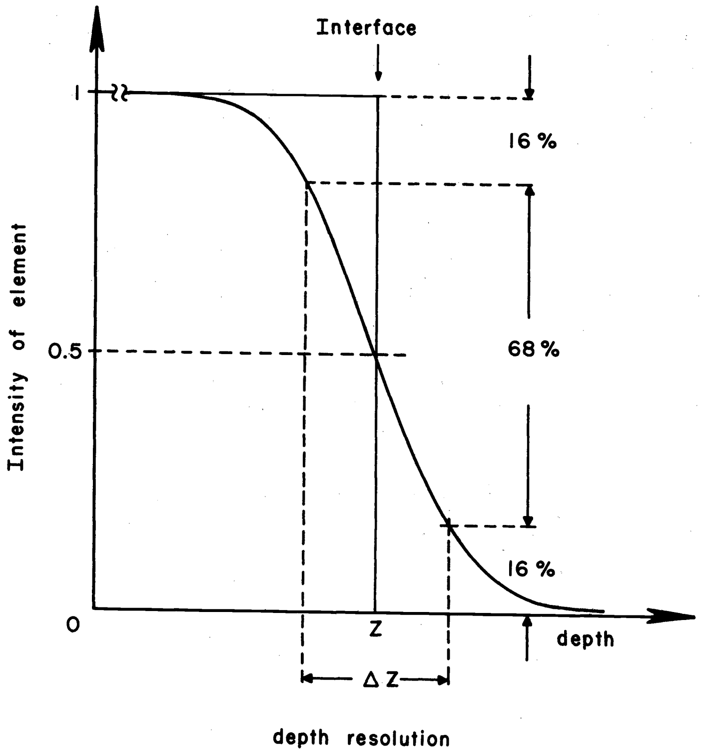

Fig. 1: Definition of Depth Resolution (according to Hofmann(4))

To clean residual adsorbed hydrocarbons and other contaminants clinging to the physical surfaces, very low energy Ar^+ bombarded with a diffuse beam is suggested. Farrell (6) has shown that at 0.1 to 1 eV and ion current density of $\lesssim$ 1 mA/cm^2 Ar^+ bombardment will remove impurities not bonded to the sample. In order to remove oxide layers, Ar^+ bombardment at 300-500 eV, at a current density of approximately 20 μA/cm^2 is suggested (7,8). It should be noted that composition changes in the experimental surface have been found for this method by Shimizu, et al. (9), and others (7,10). Morphology and coordination changes are also likely.

REPORTING OF EXPERIMENTS

The parameters and general information needed to define the experiment performed, such that the results may be properly interpreted and/or reproduced by other workers, constitute the minimum information which should be reported in a scientific paper.

For all of the techniques included in this discussion, the following information should be supplied in a paper:

1. The method of preparation of the sample, including cutting, polishing (material, size and methods), mounting and cleaning, indicating any special treatment such as annealing or fracture under ultra high vacuum.
2. Vacuum in the sample chamber and other chambers of importance under operating conditions (unit: N/m^2) and the method of achieving the vacuum and of determination the pressure.
3. Source of all materials, and their form.
4. Temperature at which the determinations were made if different from room temperature. If the sample is heated (either by external energy input or due to the experiment) the form, extent and characteristics of that heating should be described; e.g., resistive tungsten wire heating of the entire sample so as to raise the sample temperature from 150°C to 500°C at a rate of 10°/min.
5. Instrumental resolution for the measured signal. The

stated, e.g. mass spectrometer m/e resolution should be stated for the m/e region in which the data were taken. If the resolution varies, the instrumental resolution for the various portions of a spectrum in which reported data lie should be reported. Mass, energy, spatial, and/or the spectrometer scanning rates (mass numbers per second or Vs^{-1}, etc.) and the integration time used for each peak should be indicated.

6. The instrumental "window", particularly in energy-measuring techniques. The window width and position should be reported (FWHM); if the width as full-width at half height maximum peak varies due to any experimental manipulation carried out during an experiment, the width vs. variable information should be included.
7. Whether a static or scanning method was used to deliver the primary particles or radiation, with the scanning information; e.g., area scanned, number of scans per area and scan rates.
8. Indicate the method of quantification (standards, calibration graphs, etc.) and all corrections made to the raw data and their magnitudes, e.g., charge-up corrections in XPS, secondary ion yield corrections in SIMS, etc.
9. The number of determinations made to obtain a reported value and the precision obtained.
10. Estimated or derived experimental error in all important derived quantities.
11. Incidence angle of the radiation or particles from the source, measured from the normal to the surface.
12. Takeoff angle of the detector; i.e., the angle from the surface normal at which the detection is accomplished. The solid angle of acceptance for the detected particle or radiation should be included.

AES -

a. The primary beam area and approximate shape, beam flux, nominal energy and FWHM of the energy distribution.

b. The instrumental value for the absolute energy of the predominant gold peaks determined on pure gold and the FWHM (full width at half maximum peak height) of the peaks.

c. Gold should be evaporated or sputter-deposited onto the sample when possible, to provide a reference in electrostatic equilibrium with the sample (11), and the predominant gold peaks should be used as a reference of each sample.

d. The numerical value of the modulation frequency.

e. For AES micrographs indicate magnification, spatial resolution, the mode (N(E) or dN/dE), the value of the modulation frequency, the time for a complete scan and if background normalization has been performed.

RBS -

a. The primary ion beam area, shape, flux, nominal energy and FWHM of the distribution.

b. The method used to calibrate the instrument for determining the areas of the peaks.

ISS -

The primary ion beam area, shape, flux, nominal energy and FWHM of the distribution.

SIMS -

a. The primary ion beam area, shape, flux, nominal energy and FWHM of the distribution.

b. The ions used in the experiment and the impurity level, including ions of the desired primary gas having a charge different from that of the majority used.

c. For ion micrographs indicate magnification, spatial resolution, thickness of sample sputtered off during exposure and changes in surface morphology.

XPS -

a. The primary X-ray beam area, shape, nominal energy, and FWHM line width.

b. The "impurity level" of other photon energies impinging on the sample.

c. Gold should be sputter - deposited on the sample when possible, to provide a reference which is in electrostatic equilibrium with the sample (11), and the gold 4f 7/2 peak should be used as a reference for each sample, particularly in making corrections for charge-up.

d. The instrumental value for the absolute energy of the gold 4f 7/2 peak and the FWHM of that peak, determined on pure gold.

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REFERENCES

1. These definitions have been adapted or taken without modification from the Definitions, Terminology and Symbols in Colloid and Surface Chemistry, Pure and Applied Chem. 31, 577 (1972).
2. These definitions have been adapted or taken without modification from the Tentative Nomenclature for Auger Electron Spectroscopy of ASTM Committee on Surface Analysis E. 42 (Chairman J. R. Cuthill, NBS).
3. J. M. Thomas, Prog. Surf. Memb. Sci., 8, 49-80 (1974).
4. S. Hofmann, Appl. Phys. 9, 59 (1976).
5. R. A. Langley, D. S. Sharp, J. Vac. Sci. Technol., 12(1), 155-59 (1975).
6. T. Farrell, J. Phys. E. (Sci. Instrum.), 6, 977-79 (1973).
7. M. L. Tarng, G. K. Wehner, J. Appl. Phys., 42, 2449-52 (1971).
8. H. S. Wildman, J. K. Howard, P. S. Ho, J. Vac. Sci. Technol., 12(1), 75-78 (1975).
9. H. Shimizu, M. Ono, K. Nakayama, Surf. Sci., 36, 817-21 (1973).
10. M. Ono, Y. Takasu, K. Nakayama, T. Yamashina, Surf. Sci., 26, 313 (1971).