Report on the 34th IUVSTA Workshop "XPS: From Spectra to Results – Towards an Expert System"

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Abstract

A summary is given of a Workshop titled "XPS: From Spectra to Results – Towards an Expert System" that was held in St. Malo, France on April 22-26, 2002 under the sponsorship of the International Union of Vacuum Science, Technique and Applications (IUVSTA). This Workshop was held to develop the structure and initial content of a possible future expert system for X-ray photoelectron spectroscopy (XPS). Following three plenary presentations, the participants met in six groups to discuss the following topics: (a) instrument and specimen characterization; (b) experimental objectives; (c) wide-scan interpretation – trial composition and structure; (d) protocols for narrow scans, instrument setup, and data acquisition; (e) reduction of narrow-scan data – chemical-state and morphology analysis; and (f) reduction of narrow-scan data – quantification. These discussions led to many recommendations for elements of an expert system for XPS. Some of these recommendations are included in this summary; additional recommendations are included in the reports of the six groups available on the internet (URL address to be added later).

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a commonly used tool for surface analysis in many scientific and technological applications. However, as far back as 1990,[1] it was predicted that as XPS became more mature and more widely available it would become constrained by a lack of available experts. This problem could be addressed by the incorporation of expert elements within a typical data system, but the information backing these elements would have to be supplied and agreed by the community of users. To set up this body of factual knowledge and best practice for XPS and the related technique of Auger-electron spectroscopy, three related Workshops have been held under the auspices of the International Union of Vacuum Science, Technique and Applications (IUVSTA):

11th IUVSTA Workshop "Auger Electron Spectroscopy: From Physics to Data" (Saint-Pierre de Chartreuse, France, 1995)[2]

22nd IUVSTA Workshop "X-ray Photoelectron Spectroscopy: From Physics to Data" (Hortobagy, Hungary, 1999)[3]

34th IUVSTA Workshop "X-ray Photoelectron Spectroscopy: From Spectra to Results – Towards an Expert System" (St. Malo, France, 2002)

We provide here a summary of the third Workshop listed above. The overall objective of this Workshop was to develop the structure and initial content of an expert system for XPS that would be based on user-specified requirements and that would include expertise and guidance from world experts. This objective was to be accomplished by achievement of consensus on sets of rules that could be incorporated into a future XPS data system.[1,4] These rules would be based on agreed best practices and procedures for particular analytical requirements and, where appropriate, particular classes of materials. The two main functions of the proposed expert

system were considered to be: (1) to guide the user in the efficient acquisition of XPS data appropriate for solution of a user-specified problem, and (2) to assist the user in the interpretation and reduction of the XPS data. Within these two main functions, self-contained modules would be called for specific purposes. It was thought that the expert system (or modules of the expert system) could operate on a stand-alone personal computer or be available in future data systems of XPS instruments.

We give information on the programme and structure of the Workshop in the following section. Most of the Workshop was devoted to discussions among six Groups that met separately to discuss different topics. We present summaries of the reports of these Groups here; their more detailed reports are available on the internet.[5] We end with a discussion and some final conclusions.

PROGRAMME AND STRUCTURE OF THE WORKSHOP

In order for the knowledge base of a future XPS expert system to have the required provenance and wide acceptability, experts with a wide diversity of experience were invited to participate in the Workshop. As indicated in Table 1, 63 scientists from 16 countries participated in the Workshop.

The Workshop was held at the Hotel de l'Univers, St. Malo, France, over the period April 21-26, 2002. The local chairman was J.-P. Langeron (France), and the local committee consisted of J.-P. Langeron, B. Dallery, and V. Pfohl. Administrative arrangements were capably provided by the French Vacuum Society, and a very successful companions programme was arranged and hosted by the late Mrs. A. Langeron.

The Workshop was co-chaired by the present authors, and the programme was developed with the assistance of an International Program Committee consisting of J. E. Castle (UK), J. T. Grant (USA), L. Kover (Hungary), E. Ollivier (France), C. J. Powell (USA), M. P. Seah (UK), and K. Yoshihara (Japan).

The Workshop began with a plenary session in which there were three invited speakers. Prof. K. Ahmad (University of Surrey, UK) spoke on knowledge management, with emphasis on best practice and the possibility of new discoveries. He considered expert systems as a precursor to knowledge management, machine learning programs (neural nets), and information retrieval systems that could provide access to textual data (as found in journals and handbooks) and databases of materials-property data that are available on the internet. Dr. E. Ollivier (European Aeronautic Defence and Space Company, France) described possible experimental objectives for an expert system. Prof. Castle proposed the use of "wizards" that could be invoked in a future XPS expert system to provide enhanced guidance to an analyst in the design of an experiment (for a specified type of material and objective) and more powerful interpretive tools.

Workshop attendees were asked to participate in extended discussions with one of the following six Groups:

A. Instrument and Specimen Characterization (Leader: Dr. M. P. Seah, National Physical Laboratory, UK)
B. Experimental Objectives (Leaders: Dr. E. Ollivier and Dr. S. W. Gaarenstroom, General Motors Research and Development Center, USA)
C. Wide-Scan Interpretation - Trial Composition and Structure (Leader: Prof. Castle)
D. Protocols for Narrow Scans, Instrument Setup, and Data Acquisition (Leader: Prof. P. M. A. Sherwood, Kansas State University, USA)

E. Reduction of Narrow-Scan Data - Chemical State and Morphology Analysis (Leader: Prof. W. S. M. Werner, Technical University of Vienna, Austria)

F. Reduction of Narrow-Scan Data - Quantification (Leader: Dr. C. J. Powell, National Institute of Standards and Technology, USA)

The leaders of each Group gave introductory presentations in a plenary session to outline the proposed work of their Groups. After this session, there was a poster session at which 32 poster papers were presented, as indicated in Table 2. These poster papers included descriptions and demonstrations of available software and databases for XPS.

On the following days, the six Groups met separately to discuss procedures, algorithms and data that might be incorporated into a future XPS expert system. The attendees were asked to think broadly about the structure and function of such an expert system, and not to consider details or issues associated with implementation. There was an intermediate plenary session at which preliminary conclusions and issues from each Group were presented and discussed, and a final session at which the work of each Group was summarized.

The Workshop was very successful. The participants were enthusiastic about their tasks, and each Group produced many recommendations. There was a good mix of experience and expertise, and a vast amount of information was contributed. This review will serve as an introduction to a wonderful collection of data and factual information concerning the use of XPS as an analytical technique.[5] The following sections give overviews of the reports from the individual Groups, as given at the meeting and then as amended and agreed by Group members later. It should be recognized that these reports are not “complete.” In the limited time available, each Group did the best job it could in fulfilling the Workshop objectives. It should also be noted

that no attempt has been made to edit the Group reports to eliminate duplicative material or to present information in a uniform format or style.

INSTRUMENT AND SPECIMEN CHARACTERIZATION: REPORT OF GROUP A

Topics Discussed

This Group discussed the manner in which an expert system could assist the user with regard to characterization of the XPS instrument (i.e., the extent to which it could be considered to be performing reliably) and to determining information on the sample (or set of samples) that would facilitate the later XPS experiments. It was presumed that the expert system would conduct an interview with the user on relevant topics; some of the suggested topics are outlined here. More details are given in the final report.[5]

Knowledge of instrumental performance

- Calibration status of the binding-energy scale
- Determination of instrumental transmission function, and subsequent checks
- Linearity of instrumental intensity scale
- Knowledge of the spatial resolution and acceptance area of the analyser

Existing Knowledge of the Sample

- Sample descriptors
- How the sample arrived at the analyst
- Sample cleaning and handling
- Prior analysis/use of several methods

Ensuring that the Instrument is Performing Reliably – Calibrations

- System health check
- Mechanical
- Sample holder
- Vacuum
- Performance check
- Optimum settings
- System configuration
- Energy calibration
- Charge compensation
- Intensity repeatability
- Intensity/energy response function
- Linearity test
- Spatial resolution
- Charge compensation
- Depth resolution
- Depth

For example, an XPS spectrum of a gold reference sample could be used to assess the flux of X-rays (and the anticipated life of the x-ray source), the presence of X-ray ghosts, possible damage to the X-ray window, detector settings, and internal scattering of electrons in the analyser.

In their discussions of the above topics, the Group drew attention to the many relevant ISO standards that could be used in the expert system to calibrate or characterize the instrument

and to provide other needed information. Table 3 shows relevant standards and technical reports developed by ISO Technical Committee 201 on Surface Chemical Analysis together with proposed standards and technical reports currently in development.

For sample descriptors, the Group pointed to the system used in ISO 14975 (Table 3). Table 4 shows examples of sample descriptors from this standard. Descriptors of this type could form the basis of a questionnaire to be used interactively with the user of the expert system.

The Group proposed use of the calibration matrix shown in Table 5. Calibrations are needed to obtain meaningful XPS data for the indicated purposes or to optimise the instrument so that it can be used efficiently (i.e., to obtain the most useful information in the time available). All of the calibrations listed in Table 5 were considered *essential*. It was recommended that these calibrations be performed at intervals of three months; scheduling of the calibrations could be arranged by the expert system for a quiet time in instrument use. For a first version of an expert system, the first five calibrations in Table 5 should be included as a high priority; the remaining calibrations should be included in later versions. It should be noted that linearity of the intensity scale was viewed as a critical issue for XPS instruments that use charge-coupled detectors.

Conclusions

The Expert System needs to operate at different levels: at least at an administrator and at the user level. It is expected that there will be many forms of the expert system at different levels of integration. One may envisage (a) a paper-based ISO-type guide, (b) a computer-based equivalent with a question-and-answer basis, (c) a computer-based system interrogating the data-capture computer, and (d) a fully integrated system. It was recommended that the development of

an expert system be phased. The development should start with simple tasks so that later enhancements can be added in a visible and constructive way.

EXPERIMENTAL OBJECTIVES: REPORT OF GROUP B

Topics Discussed

Group B spent some time discussing the many different experimental objectives that users might have in undertaking an analytical investigation. They were assisted by the results of a questionnaire that had been prepared by Dr. Ollivier and published on a web site and made available to participants (and others) prior to the meeting. They attempted to avoid topics that would be addressed by Group A and assumed that XPS would have been selected by the user as the technique required to solve the particular problem or sample. More details are given in the final report.[5]

Responsibilities of the Analyst

The report from this Group made use of text boxes rather than lists; this approach avoids ascribing priorities to items that are otherwise fully equivalent. Figure 1 illustrates major responsibilities of an XPS analyst. The preliminary consultation with the supplier of the sample will be used to identify any particular problems likely to arise, e.g. susceptibility to vacuum or radiation-induced degradation. The analyst will be responsible for the calibration state and the overall performance of the XPS instrument. Taking into account the input from the left-hand text boxes, he/she will set up the wide- and narrow-scan data-acquisition sequences. The analyst will then make an evaluation of the XPS data and produce a report.

Further details of the analyst's tasks and of likely interactions with his/her customer are shown in Fig. 2. It is clear from this flow chart that examination of a typical sample normally proceeds in an interactive manner, with emphasis often being given to the cost-effectiveness of the work and the possibly limited budget available. It is also clear that the desirable time at which to make an initial assessment of the work plan comes at the end of the survey scan which, in many cases, might be sufficient to meet the needs of the client.

Specimen Forms and Materials Types

The complexity of the interacting factors in XPS analyses is due to the many different forms of specimen materials and the variety of material types that may be encountered as well as to the different XPS experiments that might be required. Figure 3a illustrates possible specimen forms, Fig. 3b shows possible material types, and Fig. 3c indicates possible XPS experiments or issues for further review.

Analytical Problems and Strategies

Table 6 gives an idea of the long and detailed discussions among this Group concerning the importance of the interaction between the analyst and his/her customers. More details of this nature and recommended XPS approaches for specific material forms and experimental objectives are available in the full report.[5]

Conclusions

An expert user has a large amount of experience in interpreting the best experimental approach for a given type and form of sample. Checklists were developed that should be useful

for less experienced analysts. These checklists could also be utilised by the designer of an expert system to set up or recommend the most cost-effective routines for analysis. Finally, the checklists could give guidance on problems likely to be encountered and on limits to the information likely to be provided by expert use of XPS to characterise the sample surface.

WIDE-SCAN INTERPRETATION – TRIAL COMPOSITION AND STRUCTURE: REPORT OF GROUP C

This Group set themselves a 'mission' and a fairly limited task. However, this process enabled them to make the firm recommendations given below. Their agreed mission was to provide a qualitative assessment of quantitative opportunity. Their task was to produce an implementable protocol for the collection and analysis of a standard XPS survey scan for the extraction of the maximum available information. This information *may* then guide the next steps in the analysis of a sample. A principal output was a flowchart (Fig. 4) illustrating the essential steps in the acquisition of a survey scan and giving decision points where rules would be needed. Initial development of the underlying rule set then guides the decision tree.

Topics Discussed

The Group considered the following topics: instrument condition, sample description, energy resolution, range of the survey scale, step size and acquisition mode, scan strategy, charge correction, peak identification and labelling, peak intensity, element-specific data, assessment and utilisation of the background, assessment and utilisation of peak intensities, assessment of the whole spectrum, output to screen, and region set-up. Recommendations for some of these topics are given below; further details are given in the full report.[5]

Instrument Condition

A major assumption underlying data acquisition is that the XPS instrument is in good operating condition (i.e., that calibrations have been made of the binding-energy scale and the transmission function, that measurements are made for conditions in which the intensity scale is linear, and that the X-ray source and photoelectron detector are operating correctly). The Group assumed that logs were maintained and that events such as open system-to-air would be included.

Recommendation: *Flag(s) should be set for instrument state and made available during the data-acquisition sequence and to the output screen if required.*

Sample Description

The format in ISO 14975 is largely satisfactory but needs augmenting.

Recommendation: *Include descriptors to indicate whether sample has been air-exposed, to indicate the elements sought, and to specify the peak to be used as a charge reference (default is unset).*

Energy Resolution

The main task of the survey scan is to detect all possible peaks in the most time-efficient manner and to *minimise* the possibly adverse impact of chemical shifts on peak recognition.

Recommendation: *The overall energy resolution should be 2 eV (as measured by the full-width at half-maximum intensity of the Ag* $3d_{5/2}$ *peak).*

Range of the Survey Scale

The range of binding energies scanned in a survey scan should be large enough to include the carbon KLL Auger peak and other potentially valuable peaks.

Recommendation: *The survey scan should cover binding energies from zero to 1150 eV for Mg Ka X-rays and from zero to 1350 eV for Al* $K\alpha$ *X-rays.*

Step Size and Acquisition Mode

The energy steps in the survey scan should be sufficiently small so that useful estimates can be made of peak areas. The fixed-analyser-transmission (FAT) mode of instrument operation should be used so that the survey scans will match any narrow-scan spectra acquired later and that background-subtraction algorithms such as QUASES[6] can be used.

Recommendation: *The step size should be 0.4 eV and the instrument should be operated in the FAT mode.*

Scan Strategy

Multiple scans (rather than a single scan for the same data-acquisition time) permit analysis of any drift in peak positions and intensities with time. Multiple scans also allow the possibility of finding convergence of the trial composition from each wide-scan spectrum (e.g., to test whether there might be sample degradation due to irradiation by X-rays).

Recommendation: *Use multiple scans and test for possible drift in peak positions and intensities. The scans could be terminated after convergence of a trial composition or after obtaining a desired signal-to-noise ratio (or after a selected maximum number of scans).*

Output to Screen

Recommendation: *An XPS expert system should provide the information listed below (in addition to the wide-scan spectrum):*

- *Warning if an instrument flag indicates a problem*
- *Evidence of sample charging during data-acquisition*
- *Evidence of composition change during data-acquisition*
- *A trial composition based simply on measured peak intensities and corresponding elemental relative sensitivity factors (and the assumption that the sample is homogeneous)*
- *Estimate of equivalent overlayer thickness using (a) the intensity of the carbon photoelectron peak and (b) the ratio of the carbon peak to the strongest substrate peak*
- *Corrected substrate composition (using the average of the overlayer thicknesses determined in the previous step)*
- *Information from the inelastic background (e.g., direction of any concentration gradients)*
- *Evidence of chemical state from presence of satellites or from Auger parameter*
- *Display of any similar spectra from the expert system (or other sources) for known compounds*

Conclusions

The operation of a prototype expert system should be tested manually on survey spectra for a wide variety of samples. Similar tests should be made of the algorithm and recommendations using existing data. Finally, tests should be made with an XPS instrument.

PROTOCOLS FOR NARROW SCANS, INSTRUMENT SETUP, AND DATA ACQUISITION: REPORT OF GROUP D

This Group was concerned with defining the information needed to create a strategy for the best use of time and resources and the means by which the user might best be guided along a recommended path.

Topics Discussed

The Group considered the design of a strategy for optimal data acquisition for desired experimental objectives (including the use of wizards to suggest measurements of satellite features or Auger peaks for specific elements[4]), regions of binding energy to be scanned, number of counts (or amount of time) required for experimental objective(s), avoidance of potential problems (e.g., overlapping peaks from different elements, adequacy of chemical shifts for expected chemical states, need to make measurements for elemental peaks before the onset of any specimen degradation, etc.), analysis of narrow-scan spectra including comparison with wide-scan spectra and presentation of spectra for subtraction of backgrounds, interactive curve-fitting or peak-shape analysis, and issues involved in computer hardware and software for an expert system as well as with communication with other resources. Recommendations for some of these topics are given below; further details are given in the full report.[5]

Data Acquisition

The Group noted that opportunities might be missed or peaks might be misinterpreted as a result of non-familiarity with the positions and characteristics of Auger peaks or satellite peaks for specific elements.

Auger Peaks

Recommendation: *A wizard should notify the user of the position and shape of likely Auger peaks (for the element(s) of interest or in the energy range of interest). This wizard might also notify the user as to whether there might be a chemical shift of the Auger peaks and whether the Auger peaks are likely to experience splitting as a result of final-state effects (multiplet splitting). The wizard should alert the user to the potential value of recording a narrow scan of a "promising" Auger region. For example, if the user is examining the carbon 1s region, the wizard might suggest examining the carbon KLL Auger region. Another example would be a recommendation to use the appropriate Auger region to obtain an Auger parameter.*

Satellite Features

Recommendation: *A wizard should be able to access a library of satellite information associated with particular shake-up and shake-off features (shake-off features are much less common and generally much broader than shake-up features), and notify the user of their likely energies. When achromatic radiation is used, it is especially important for the wizard to draw attention to X-ray satellites.*

Recommendation: *A wizard should monitor possible change in the relative intensities of the satellite feature and the associated main peak as a monitor of potential decomposition. There is no obvious way of distinguishing between shake-up, shake-off and multiplet splitting. In the case of identified decomposition, the wizard should suggest possible decomposition reactions, and*

encourage the user to examine other appropriate spectral regions (e.g., to note any change in the metal-to-oxide ratio).

Recommendation: *A wizard should keep a record of the relative areas of a satellite peak and the associated main peak that would prompt the user to include the areas of both satellite and main peaks in any subsequent quantification.*

Regions of Binding Energy to be Scanned: Peak Referencing

Recomendation: *The binding-energy scale of the instrument must be calibrated. Reliable measurements of binding energies for insulating samples is generally difficult (the measurements have larger uncertainties), but referencing of measured peaks to the carbon 1s peak for adventitious hydrocarbon (with a binding energy of 284.6 eV or some other reported value that must be stated) continues to be the most universal energy reference. Other reference methods can present problems; for example, gold decoration can cause decomposition, and must be applied with caution. The use of energy differences is very effective. For example, the shift between a metal and its oxidized species is a valuable approach.*

Recommendation: *Always record the binding energy of the carbon 1s peak.*

Recommendation: *A wizard should conduct an interview with the user so that the wizard could identify energy differences between appropriate peaks (e.g., for peaks from a metal and its oxide, note the chemical shift(s)), look for evidence of differential charging in the sample, and suggest biasing of the sample to isolate species with different electrical conductivities.*

Number of Counts (or Amount of Time) for Experimental Objective(s)

Recommendation: *A wizard should suggest the appropriate energy window for recording a particular elemental peak, the number of data points, the choice of analyser operating conditions, sample-damage considerations, and the measurement time (number of counts) to acquire a spectrum with the needed signal-to-noise ratio. The wizard would also suggest that additional data be acquired in the nearby background regions at lower and higher energies with an optimal data-acquisition strategy. The background data would then be combined with the peak data so that the composite spectrum could be analysed. It is recommended that analysts report the different data-collection times for different parts of a spectrum.*

Avoidance of Potential Problems

There are various unfortunate overlaps of peaks from certain elements. Artefact peaks may also arise from unwanted sources of electrons (e.g., a mass spectrometer attached to the instrument).

Recommendation: *A wizard should advise the analyst to use alternative X-ray sources and different peaks (e.g., Auger peaks and weaker photoelectron peaks) to minimize accidental overlaps of major peaks from the elements expected in the sample.*

Interactive Curve-Fitting or Peak-Shape Analysis

The output of a curve-fitting analysis should display the total fitted profile superimposed on the original (unaltered) experimental data, the fitted components, and the background. It is helpful to show residuals. Curve-fitting is only meaningful if it is performed in a chemically meaningful way.

Recommendation: *A wizard should give guidance (from an updateable database) on expected chemical shifts and other spectral features (satellites) associated with the elements of interest.*

Recommendation: *A wizard could compute a second-derivative spectrum to give guidance on the approximate number of components in a spectrum containing overlapping peaks and their approximate peak positions.*

Recommendation: *A wizard should provide information on background models, the appropriate choice of end points for the selected background model, and the choice of fitting function for the expected chemical species.*

Recommendation: *Other numerical methods such as deconvolution, factor analysis, pattern recognition, and spectral addition or subtraction may be helpful.*

REDUCTION OF NARROW-SCAN DATA – CHEMICAL-STATE AND MORPHOLOGY ANALYSIS: REPORT OF GROUP E

Topics Discussed

This group discussed finding and identifying chemical states using qualitative and quantitative line-shape analysis, identifying sample morphology, and obtaining information on the compositional depth profile. Recommendations for some of these topics are given below; further details are given in the full report.[5]

Qualitative Line-shape Analysis

The information required to be 'known' to the expert system would be assembled from data characterising the specimen (as received from the client), the set-up of the instrument (e.g., the selected X-ray source and the analyser operating conditions), and information from the

relevant database(s). The system would then combine this information with information gained by self-interrogation of the spectra during and subsequent to data-acquisition. In this manner, the following checklist of actions would be created.

- Elemental composition
- X-ray source
- Information from database
    - Photoelectron lines as well as chemical states of these
    - Auger lines
    - Satellites
    - Ghost satellite lines (appropriate to X-ray source and expected peaks)
- Peak-finding procedure (for expected peak-detection limit)
- Classification of intensities of found peaks
- Identification of peaks by comparison with data base
- Consideration of overlapping peaks
- Output showing number of identified peaks (with chemical information)
- If most but not all peaks have been identified, give alert and proceed
- If strongest peaks have not been identified, alert and stop
- If there is an inconsistency with prior information, alert and stop
- If all peaks have a similar shape (perhaps due to differential charging), alert and stop
- If multiple chemical states for an element have been detected, follow recommendations from Groups C and D
- Stop if customer´s questions have been answered
- Proceed with quantitative line shape analysis

The Group noted that correct identification of found peaks requires calibration of the instrumental binding-energy scale, use of appropriate reference peaks for non-conducting samples, and consideration of relevant uncertainties in measured and reference binding energies.

Quantitative Line-shape Analysis

The following checklist identifies the sequence of actions that might arise from a quantitative line-shape analysis.

- Elimination of X-ray satellites and inelastic background
  - Use straight-line background for a homogeneous insulator
  - Use Shirley background (although use straight-line background if Shirley background gives unsatisfactory results)
  - Include in peak fit
- Methods for peak fit:
  - Linear least-squares fit
  - Factor analysis (needs to be further developed for shifted peaks)
- Use of synthetic peaks or reference peaks (from local measurements or an external database)
- Use of prior information to constrain fitting algorithm
- Output with number of components and positions, widths, and heights of each component
- If all peaks have been identified, proceed
- If components are inconsistent with prior information, alert and stop
- If the number of components is different from prior qualitative analysis, return to qualitative analysis

Identifying Sample Morphology

Practical samples can have many different types of surface morphologies (e.g., surface roughness, lateral inhomogeneities, depth inhomogeneities, islands, nanoparticles (with diameters of the order of the photoelectron inelastic mean free path), separated phases, and high-surface-area materials (e.g., powders and catalysts)) and combinations of these morphologies. Possible goals of XPS measurements could be to provide information on the sample morphology, avoid erroneous data interpretation resulting from the effects of morphology, or to acquire chemical and/or quantitative information despite morphological complications using an appropriate model.

If the feature size is smaller than the analysis area (the typical case in XPS), the amount of information from XPS experiments is limited, as indicated in Table 7. In general, these analyses require additional thought, data-acquisition time, and attention to data interpretation and quantification. In terms of quantitative modeling, simple geometric models accounting for the influence of the morphology on the measured spectra have proven to be effective for many morphologies. The acquisition of spectra at two or more emission angles is qualitatively useful for checking some aspects of sample homogeneity (or lack thereof).

Recommendation: *Acquire survey spectra at two emission angles (e.g., at 0° and 60° with respect to the surface normal). If there is no variation of the ratio of these spectra with binding energy, the sample is homogeneous or consists of adjoining phases and standard quantification methods can be applied. If there are large variations of this ratio, the sample morphology will affect the quantitative analysis.*

Recommendation: *The effects of surface roughness are minimised if spectra are measured at emission angles between 35° and 55°.*

Recommendation: *The characteristics of surface islands can be determined from an analysis of the spectral lineshape (including the inelastic background) or from angle-resolved XPS.*

Recommendation: *For high surface-area materials (with a surface area greater than 70m^2/g), information on surface composition, particle shape and diameter, and particle concentration can be obtained with a suitable model.*

Compositional Depth Profile

Recommendation: *Information on compositions and thicknesses of thin-film structures can be obtained from ratios of overlayer and substrate peak intensities, an analysis of the spectral lineshape (including the inelastic background), and angle-resolved XPS. The latter two approaches can be used to derive limited composition-versus-depth information for samples in which the composition is changing continuously with depth. Emission angles between 0° and 60° should be used in these experiments.*

Conclusions

It is possible to define checklists by which basic data on composition and morphology can be obtained. The manner and sequence by which the interpretation is made augments and overlaps recommendations from Groups C, D, and F.

REDUCTION OF NARROW-SCAN DATA – QUANTIFICATION: REPORT OF GROUP F

Topics discussed

This Group considered identification of chemical state, quantification (determination of composition, film thickness, and spatial variation of composition), data sources and issues in estimation of uncertainties, and new/improved methodologies for XPS. Recommendations for some of these topics are given below; further details are given in the full report.[5]

Identification of Chemical State

The Group discussed methods to detect possible compositional variations with lateral position on the sample surface and with depth. If only one compound is identified or expected for a particular phase in the sample, the following checklist gives a guide for assessing the initial (trial) sample composition.

- Estimate composition for an identified phase from peak intensities
- Compare this composition with that expected (if bulk composition is "known")
- Consider what this estimated composition implies for chemical shifts, satellites, energy-loss features, and valence-band spectrum
- If only one compound is present, compare measured spectrum with a reference spectrum or with a calculated spectrum (if available).

If more than one compound is present in the sample, chemical shifts should be examined for different possible stoichiometries, the positions and shapes of any satellites should be investigated, the measured survey spectrum should be compared with appropriate reference spectra, and tests should be made to determine whether the measured spectrum is a linear

combination of spectra for expected or suspected compounds. In the future, the measured spectrum should be compared with libraries of spectra using pattern recognition techniques.

Quantification (Composition, Film Thickness, Spatial Distribution of Composition)

Quantification begins with measurements of peak intensities. For a single observed peak (single chemical state), it is often convenient to use either a Shirley or a straight-line background, particularly if intensity measurements are required for a series of similar samples or if the same sample is being processed in some manner; the absolute intensities may vary depending on how the background-subtraction procedure is implemented. The use of a physical model to describe inelastic scattering can be used for background subtraction, and will provide intensities of better reliability although spectra will then have to be acquired over a wider energy range.

Several approaches are possible for determining compositions from measured intensities:

(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.

(iii) Direct comparison of spectra (e.g., for alloys) with reference spectra.

Recommendation: *Method (i) above is a simple means to obtain an approximate composition. Method (ii) should be used to obtain a more accurate composition. Method (iii) can be used if suitable reference spectra are available.*

Peak-shape analysis and angle-resolved XPS are useful approaches for determining composition as a function of depth. These techniques can also be used to determine thicknesses of overlayer films; film thicknesses can also be obtained from ratios of substrate and overlayer peak intensities for a single emission angle.

For determinations of elemental composition or of chemical state as a function of lateral position on the sample, simple measures of peak intensity are often required to minimize data-acquisition time. Advanced numerical methods (e.g., multivariate image analysis) have been developed for intensity classification and analysis as well as for visualization of the results. For such measurements, the analyst should be aware of the analysis area for the chosen operating conditions.

Data Sources and Issues in Estimation of Uncertainties

Uncertainties in derived binding energies may arise from uncertainties arising from (i) the calibration procedure (e.g., ISO 15472), (ii) possible drifts of the energy scale since the calibration, and (iii) charging of a non-conducting sample.

Recommendation: *Uncertainties (i) and (ii) above should be provided to the user by XPS manufacturers and software developers.*

The instrumental intensity scale (or intensity-energy response function) may change with time due to changes in detector efficiency (both in absolute value and in the variation of efficiency with energy). The uncertainty of measurements of peak intensities will depend in part on the background technique used and on counting statistics. It should be noted that the intensity uncertainty depends on how the intensity values are used (i.e., if the user is interested in absolute values or relative values).

Recommendation: *The instrumental intensity scale should be calibrated at regular intervals with software available from the UK National Physical Laboratory.*

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

The electron inelastic mean free path (IMFP) is a useful parameter for describing effects of inelastic electron scattering in a material. IMFPs have been calculated for a limited number of materials from experimental optical data and determined from measurements of elastic backscattering coefficients. IMFPs can be estimated from predictive formulae; these data are also available from a NIST database.

The electron effective attenuation length (EAL) is needed for the determination of overlayer-film thicknesses (rather than the IMFP). Published EALs derived from measurements of photoelectron or Auger-electron intensities as a film was deposited on a substrate often have large uncertainties because of the generally unknown morphology of the overlayer film. EALs can be obtained from a NIST database or the predictive formula of Seah and Gilmore.

The electron mean escape depth (MED) is a useful measure of surface sensitivity in XPS. MED values for specific materials and experimental conditions can be conveniently obtained from the NIST EAL database.

Two parameters provide useful corrections for effects of elastic scattering on determinations of surface composition: (i) Q_x is a factor describing reduction of photoelectron intensity ($Q_x < 1$), and (ii) β_{eff} is the effective photoionization asymmetry parameter. Values of these parameters can be obtained from the NIST EAL database or a predictive formula developed by Seah and Gilmore. Both parameters should be used in equations to give the surface composition (for a homogeneous sample).

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. In addition, the use 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, however, 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.

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

An XPS spectrum often consists of two or more peaks that may overlap by varying amounts.

Recommendation*: Software should provide estimates of uncertainties for the 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 copper compounds.

Conclusion

Considerable information for the establishment of a rule base for an expert system is already available in the literature and in published standards and methodologies. The report of this Group gives guidance on where this information can be found.[5]

DISCUSSION

XPS is an information-rich spectroscopy that requires considerable interpretative effort if it is used to describe fully the surface composition and morphology of an unknown sample. Nevertheless, XPS remains the most cost-effective technique for obtaining such information. The XPS experts assembled in St. Malo were in no doubt that much of the necessary physical and chemical theory underlying the interpretation is sufficiently well understood, but the discussions showed that this theoretical understanding and the necessary practical knowledge for efficient XPS measurements and interpretations are widely distributed through the user community. They were in no doubt that new or infrequent users of XPS could be greatly assisted by the incorporation of agreed elements of this knowledge into the data systems used with XPS instruments. Such assistance would be of considerable value in guiding the user to make appropriate measurements for different types of samples and different analytical problems. Similar assistance would also be of value in subsequent analyses and interpretations of the acquired data, and in ensuring that all necessary data were available. Given that XPS is an expensive and relatively time-consuming technique, it is important that the spectroscopic measurements be limited to those necessary to meet the analytical objectives. Whether or not these objectives are realistic for particular sample forms and material types could also be assessed by an expert system.

FINAL CONCLUSIONS

The discussions in St. Malo ranged over many aspects of XPS analyses of the surface of an unknown sample, as indicated by the relatively brief summaries here. The more detailed reports on the web sit[5] give a consensus view of sound advice that can be utilised by software writers who might wish to incorporate expert-agreed elements of an expert system into integrated

or stand-alone data systems. We also believe that the recommendations from the St. Malo Workshop will become a valuable source of "best practices" in XPS and be useful as an educational resource for both novice and experienced users.

Acknowledgments

The authors are greatly indebted to the participants of the St. Malo Workshop (Table 1) on whose work this report is based.

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3. Kover L. *Surf. Interface Anal*. 2000; **29**: 671.
4. Castle JE. *Surf. Interface Anal.* 2002; **33**: 196.
5. Internet URL for final reports to be added later (when known).
6. Commercial products are identified to specify experimental procedures. This identification does not imply endorsement or recommendation by the National Institute of Standards and Technology.

Table 1. List of participants at the 34th IUVSTA Workshop.

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D. R. Baer (USA)
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C. Blomfield (UK)
D. Briggs (UK)
C. E. Bryson (USA)
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S. W. Gaarenstroom (USA)
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M. Green (UK)
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L. Vanzetti (Italy)
J. Vegh (Hungary)
P. Weightman (UK)
W. S. M. Werner (Austria)
R. K. Wild (UK)

Table 2. List of poster papers at the 34th IUVSTA Workshop.

---

(1) *K. Robinson*, "Avantage Data System – An Overview"

(2) *M. Green, P. Grossman, and J. Westermann*, " EIS: Software for Electron and Ion Spectroscopy"

(3) *J. Westermann, M. Sander, D. Funnemann, and S. Pringle*, "High Count-Rate Detectors in High-Resolution Electron Spectrometers"

(4) *P. Ruffieux, P. Schwaller, O. Groening, L. Schlapbach, P. Groening, J. Westermann, Q. C. Herd, and D. Funnemann*, "Experimental Determination of the Transmission Factor for the Omicron EA 125 Electron Energy Analyser"

(5) *S. Mähl*, "Architecture and Functionality of SpecsLab: The Acquisition and Processing Software from SPECS"

(6) *J. Vegh*, "XPS4XPS: A Possible Implementation of an Expert System for XPS/AES"

(7) *B. V. Crist*, "The "SpecMaster" XPS Spectral Database System and Spectral Data Processor (SDP) v3.0"

(8) *M. Jo*, "Program for Background Optimization"

(9) *S. Tougaard*, "XPS-Quantitation: QUASES Algorithms I, II, III"

(10) *S. Tougaard*, "XPS-Quantitation: QUASES Algorithms IV, V"

(11) *W. Smekal, W. S. M. Werner, and C. J. Powell*, "Simulation of Electron Spectra for Surface Analysis (SESSA)"

(12) *W. S. M. Werner*, "Partial Intensity Analysis: A Universal Method for Inelastic Background Analysis of Electron Spectra"

(13) *A. Schnellbügel and R. Anton*, "Quantitative Analysis of X-ray Photoelectron Spectra of Rare Earth Fluorides"

(14) *M. Mohai and I. Bertoti*, "Calculation of Layer Thickness on Curved Surfaces by XPS MultiQuant"

(15) *R. Hesse, T. Chasse, and R. Szargan*, "UNIFIT 2002 – Spectrum Processing and Analysis Software of Core Level Photoelectron Spectra"

(16) *C. J. Powell and A. Jablonski*, "NIST Data Resources for Surface Analysis by AES and XPS"

(17) *A. Jablonski*, "Software for Determination of the IMFP from Elastic Peak Intensity"

(18) *D. Briggs,* "The XPS of Polymers: CD-ROM Database from SurfaceSpectra LTD"

(19) *G. Speranza, R. Canteri, and M. Anderle*, "Some Considerations About the Analysis of Polymeric Materials by XPS"

(20) *N. Cioffi and L. Sabbatini*, "Simple Equations for Curve-Fit Data Treatment to Obtain Quantitative Information on Polymer Structure"

(21) *D. R. Baer*, "Practical Aspects of Surface Charge Control and Charge Correction in XPS: Current Art and Understanding and a Proposed ISO Standard on Reporting of Methods Used for Charge Control and Charge Correction (ISO 19318)"

(22) *C. E. Bryson*, "Expert System for XPS – Surface Potential Control"

(23) *S. Oswald, R. Reiche, and S. Baunack*, "Application of Factor Analysis in Electron Spectroscopy"

(24) *J. C. C. Day and R. K. Wild*, "Towards an Expert System – A Practical Approach"

(25) *S. Tanuma*, "The Use of Experimentally Determined Relative Sensitivity Factors for Quantitative Analysis by XPS"

(26) *J. Toth*, "Algorithm for Automatic Chemical State Determination by XPS"

(27) *L. Kover*, "Deriving Chemical Information from X-ray Induced Electron Spectra"

(28) *M. Kurth and P. C. J. Graat*, "Quantitative Analysis of the Plasmon Loss Intensities in XPS Spectra of Magnesium"

(29) *L. Vanzetti, E. Iacob, M. Barozzi, D. Giubertoni, M. Bersani, and M. Anderle*, "X-ray Photoelectron Spectroscopy of Nitrided Silicon-Silicon Oxide Interface"

(30) *E. Ollivier*, "Theme B: Experimental Objectives for an XPS Expert System"

(31) *C. Blomfield, A. Roberts, and S. Hutton*, "Vision Data System – An Overview"

(32) *A. Tanaka*, "Practical Transmission Correction for XPS Analyzers with a Self-Consistent Transmission Function"

Table 3. International standards, proposed international standards (currently in draft form), technical reports (TRs), and proposed technical reports (currently in draft form) relevant to XPS developed by ISO Technical Committee 201 on Surface Chemical Analysis.

Number[a]	Title[b]
ISO 14975: 2000	SCA – Information formats
ISO 15472: 2001	SCA – XPS – Calibration of energy scales
ISO TR 15969: 2002	SCA – Sputter depth profiling – Measurement of sputtered depth
ISO 18117 (D)	SCA – Handling of specimens prior to analysis
ISO 18118 (D)	SCA – AES and XPS – Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials
ISO 18156 (D)	SCA – AES and XPS – Determination of lateral resolution
ISO TR 18392 (D)	SCA – XPS – Procedures for determining backgrounds
ISO TR 18394 (D)	SCA – AES – Derivation of chemical information
ISO 19318 (D)	SCA – XPS – Reporting of methods used for charge control and charge \ correction
ISO TR 19319: 2003	SCA – AES and XPS – Determination of lateral resolution, analysis area, and sample area viewed by the analyser
ISO 20341(D)	SCA – SIMS – Method for estimating depth resolution parameters with

	multiple delta-layer reference materials
ISO 21270 (D)	SCA – X-ray photoelectron and Auger electron spectrometers – Linearity of intensity scale
ISO 22335 (D)	SCA – Depth profiling – Measurement of sputtering rate: Mesh-replica method with the use of a mechanical stylus profiler
ISO 22474 (D)	SCA – AES and XPS – Guide to methods for detecting peaks
ISO 24236 (D)	SCA – XPS – Repeatability and constancy of intensity scale

[a]D: Draft document of a proposed international standard or technical report.

[b]SCA: Surface chemical analysis.

Table 4. Examples of possible sample descriptors (based on ISO 14975).

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host_material = InGaAs or ultra-thin metal layer on a thick SiO_2 layer on Si [a generic text description]

IUPAC_chemical_name = polyethylene

chemical_abstracts_registry_number = 9002-88-4

host_material_composition = C2H4 (text showing principal elements)

bulk_purity = 99.5 mass%

known_impurities = O, 0.3 mass%; N, 0.1 mass%

structure = crystal type and orientation, fracture surface, phase information, crystal size, crystal texture, layering, particulates, etc.

homogeneity = homogeneous, inhomogeneous or unknown

crystallinity = amorphous, single crystal, polycrystalline or unknown

material family = metal, inorganic, organic, polymer, semiconductor, biomaterial, composite, superconductor, etc.

special material class = rod, sheet, single-layer film, multi-layer film, sintered, wafer, powder, fibre, etc

*ex-situ prepara*tion = polished, cleaved, prepared with focused ion beam, powder, compacted, acetone degreased, etc.

Table 5. Calibration matrix indicating procedures to be used to check the indicated parameters and the importance of these parameters for the indicated XPS measurements.[a]

Parameter	Calibration Procedure[b]	Chemical State	Low-level Detection	Quant-ification	Layer Thickness	Nano-structure
Binding Energy	ISO 15472	XX		X		X
Intensity repeatability & constancy	ISO 24236		XX	XX	X	X
Intensity/energy response function	NPL software			XX	X	XX
Intensity linearity	ISO 21270	X		XX	X	XX
Energy resolution versus intensity	own procedure	X	XX	X	X	X
Ion gun & Sputter rate	ISO 15969 ISO 22335 CRM BCR 261				XX	XX
Depth resolution	CRM BCR 261 NIST 2135				XX	XX
Spatial resolution	ISO 18156 ISO 19319				X	XX
Sample stage x, y and z; orientation of spectrometer, etc; and angular resolution for ARXPS	own procedure		X	X	XX	X

[a]X = generally important, XX = generally very important.

[b]The recommended calibration procedures include use of ISO documents (Table 3), software from the UK National Physical Laboratory (NPL), or certified reference materials (CRMs) available from the European Institute for Reference Materials (BCR) or from the National Institute of Standards and Technology (NIST).

Table 6. Examples of types of problems often identified by customers and of corresponding issues that need to be addressed in XPS analyses.

Types of problems from customer:	Consequences
Surface contamination	• **Uniform vs. patchy** • **Attenuation of bulk intensities** • **Presence of expected or unexpected material**
Composition (elemental)	• **Surface vs. bulk** • **May only need widescan** • **How much accuracy?**
Composition (chemical state, oxidation state)	• **Nearly always requires narrow scans** • **The chemical state result is only from the surface, not the bulk** • **Binding energy matches difficult for charging specimens**
overlayer thickness(es) & composition(s)	• **Angle resolve if < 5 nm** • **Sputter etch if > 5 nm** • **Rough specimens very difficult**
surface vs bulk, surface segregation, enrichment	• **Information depth issues**
presence or absence of something	• **how many samples?** • **Elements, chemical states expected at what concentration?**
Lateral inhomogeneity	• **domain size vs. analysis area**
valence band, electronic state, band bending	• **surface may not be representative of bulk** • **effect of specimen handling/transport**
Evaluate a surface process (cleaning, plasma, wear, etc.)	• **many specimens possible** • **sample-set selection important**
Adhesion failure	• **mating surfaces** • **lateral inhomogeneity**
Color, haze	• **may be much thicker than analysis depth, often below the surface, low probability of success**
residue	• **A bulk type of analysis**

Table 7. Summary of information on sample morphology that can be obtained from XPS experiments. [a]

Sample morphology	Information on morphology parameters from XPS	Information on surface composition from XPS
roughness	no	possible
islands	yes	possible
high surface area materials	yes	possible
separated phases	in some cases	in some cases
nanoparticles	no	possible
depth distribution	yes	yes

[a]yes = in principle, yes, but the user needs to be aware that the analysis will require expert assistance and will be time consuming and costly.

no = in principle, yes, but there are other analysis techniques that will solve the problem faster, cheaper, and more reliably.

possible = in principle, yes, but the associated uncertainty may be large, and may require expert assistance.

in some cases = in principle, yes, but not always.

Figure Captions

Fig. 1. Major responsibilities of an XPS analyst.

Fig. 2. The interactive nature of decisions taken by the analyst.

Fig. 3. Examples of issues to consider taken from the report of Group B. a) Form of samples, b) material types, c) XPS options. The shaded boxes indicate material types for which specific consequences and proposed actions are given in the full report.[5]

Fig. 4. Recommended selection of parameters and flow diagram for a survey scan.

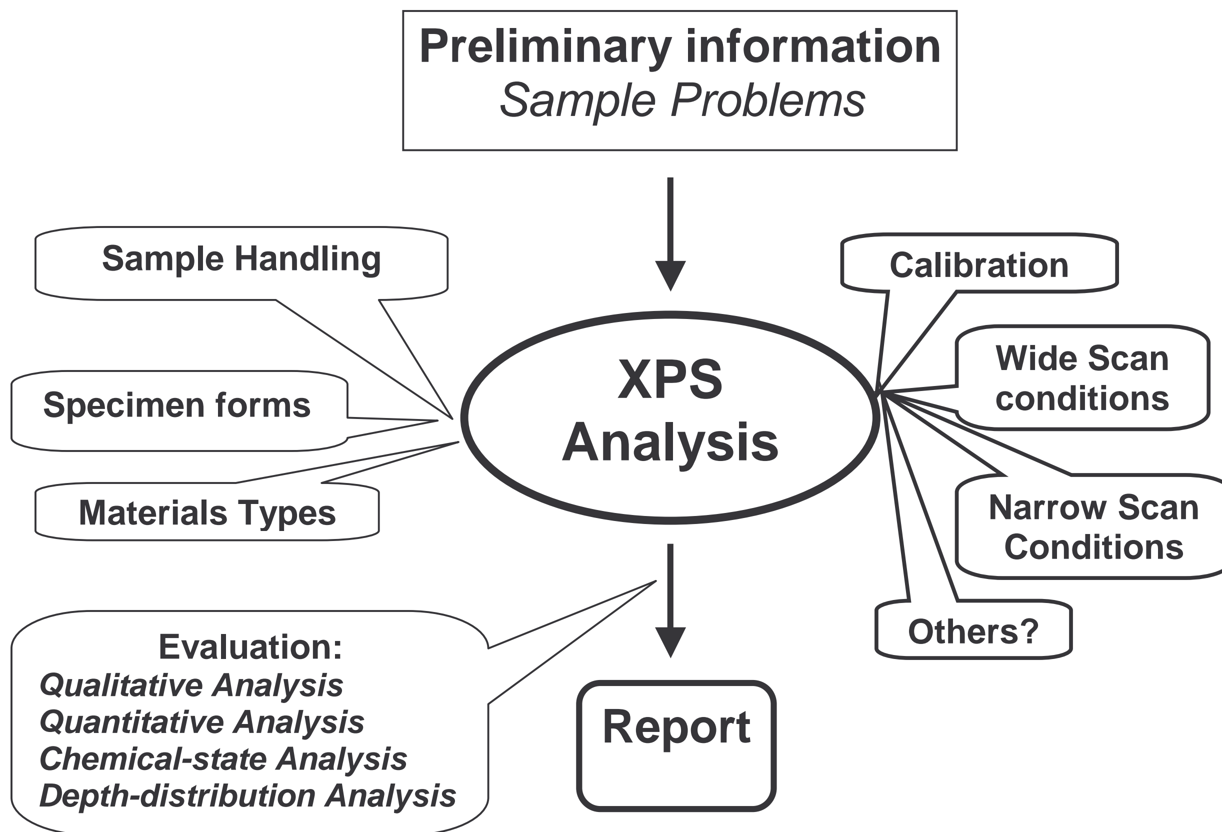

Figure 1. Major responsibilities of an XPS analyst.

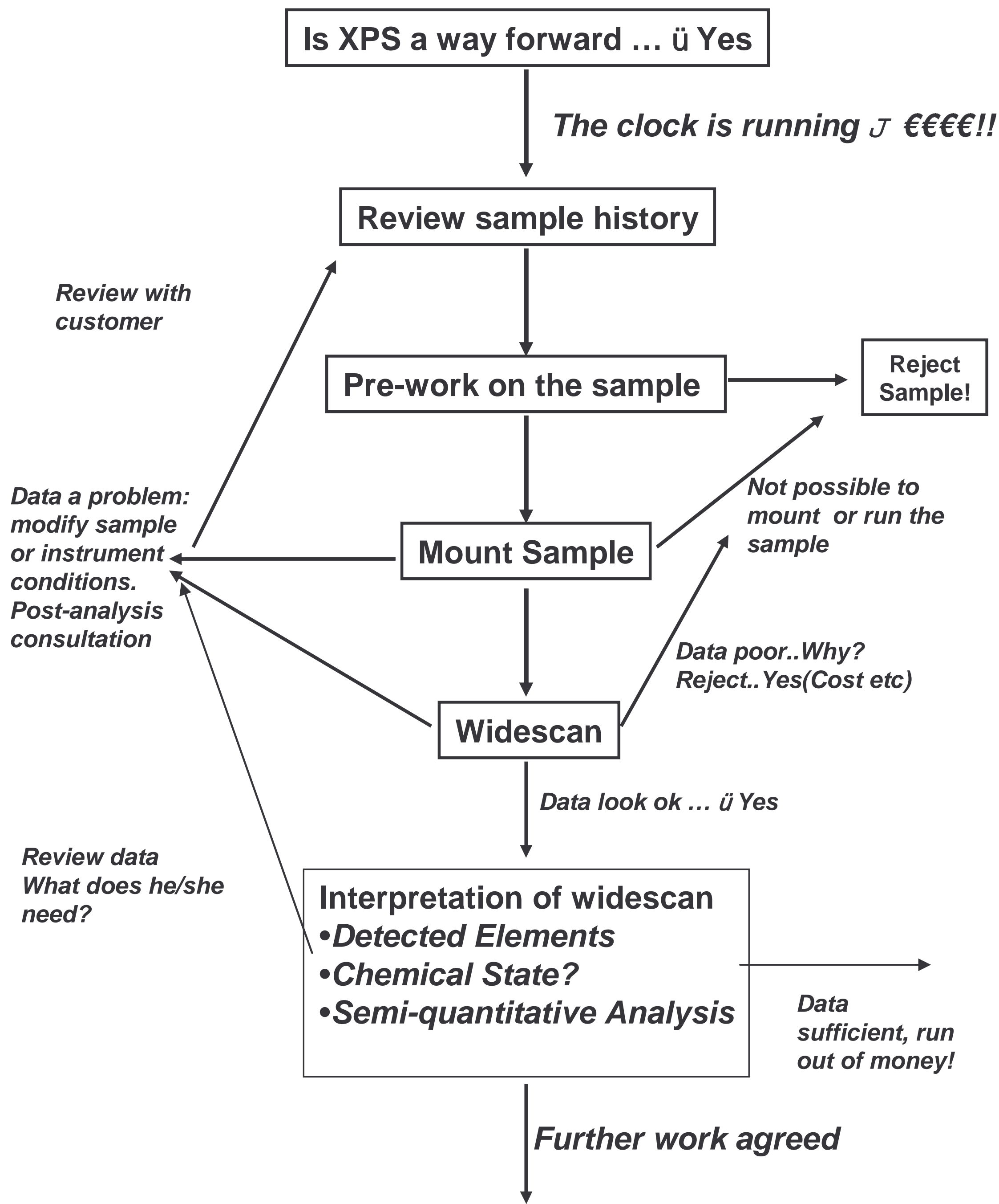

Figure 2. The interactive nature of decisions taken by the analyst.

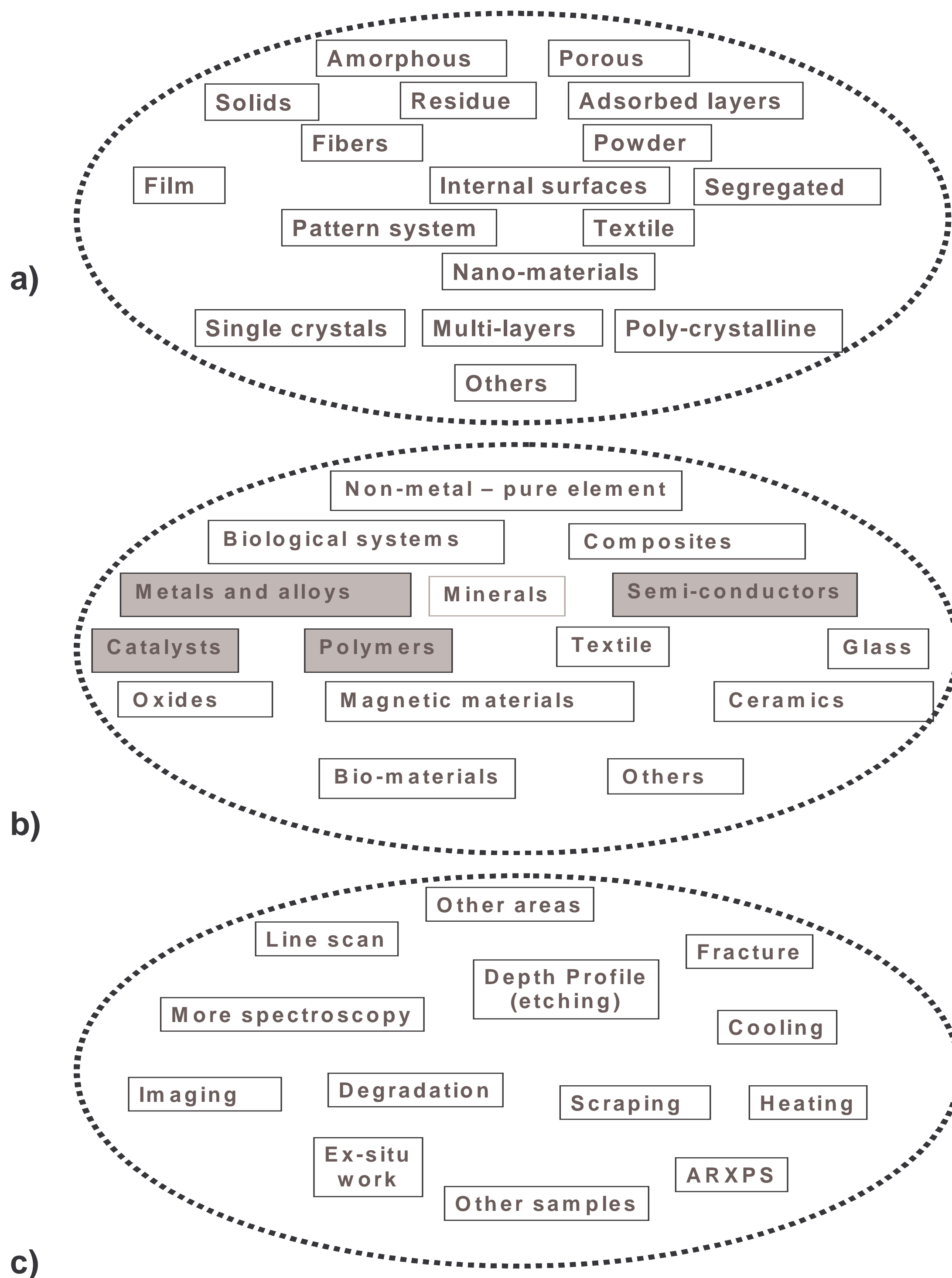

Figure 3. Examples of issues to consider taken from the report of Group B. a) Form of samples, b) material types, c) XPS options. The shaded boxes indicate material types for which specific consequences and proposed actions are given in the full report.[5]

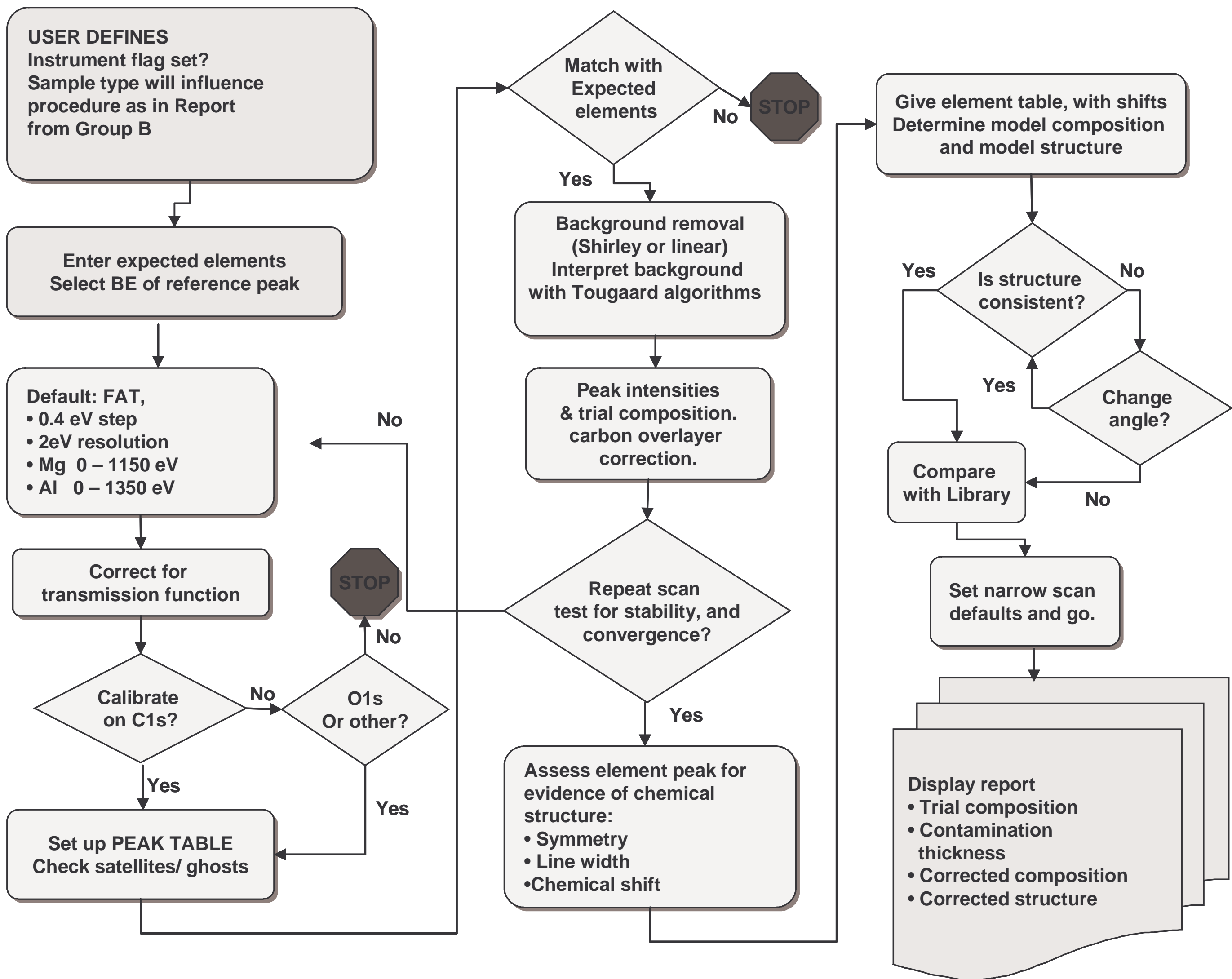

Figure 4. Recommended selection of parameters and flow diagram for a survey scan.