XPS Workshop from Spectra to Results - Towards an Expert System@

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Final Report of Group D

Protocols for narrow scans, instrument setup, and data acquisition

Participants:

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Participants from Groups A and B who joined the group on Wednesday:

Donald BAER, Pacific Northwest National Laboratory, USA
Chris BLOMFIELD, Kratos, UK
Alan CARRICK, Acolyte Science, UK
Kevin ROBINSON, Thermo VG Scientific, UK
Janos VEGH, MTA Atomki, Hungary

Participants from other Groups who joined the group on Thursday:

John GRANT, on loan from the University of Dayton, USA
Andrew PROCTOR, Intel Corporation, USA

Charge of the Group and its Recommendations

<u>Overview Issues</u>

The results of the Workshop might be implemented:

! **The instrument manufacturers might consider the issues raised in the workshop and include AExpert Systems@ in their software.**

! **IUVSTA might apply for funding from international funding agencies for support for collaborative efforts to implement the AWizards@ necessary for the development of an AExpert System@. This effort requires a team with interests over a wide range of instrumental areas and surface chemistries and should include representatives of the Instrument Manufacturers.**

Communication between an Aexternal@ or Ainternal@ Expert system and an instrument and other considerations.

Other overall issues were:

! Group recommends that a version of the software must be provided that runs on the most widely used hardware and software systems.

! The expert system should be designed to ensure that other activities on the host computer are not taking large amounts of computer time, and the expert system itself should be designed to make the most efficient use of the computer system. Thus appropriate programming that avoids code that continually monitors task works well. The AWizard@ program should monitor other tasks on the computer and recommend user action (e.g. close CAD programs when collecting data).

! Some computing capability should be included within the instrument electronics.

! Direct links via internet provides considerable opportunity for compatibility with expert systems.

! **Commercial Acquisition Software should have the capability of communication with other external software. For example an external program that could represent an expert system might also interact with the software controlling the instrument.**

! An agreed external communication protocol should be developed, and this protocol should have the capability of real time data transfer, and delayed data transfer (e.g. transferring data one scan at a time).

! An existing communication protocol will be distributed to the group to provide an example of a current working system, which might form the basis for a new agreed communications protocol.

! Consideration should be given to a distributed expert system.

Providing Extra Experimental Information for storage with the datafile.

Future expert systems, communicating with manufacturer software via the appropriate communications protocol, should monitor, and record in a data file:

! Instrument pressure.

! Any partial pressure data collected by quadrupole mass spectrometers attached to the spectrometer vacuum system.

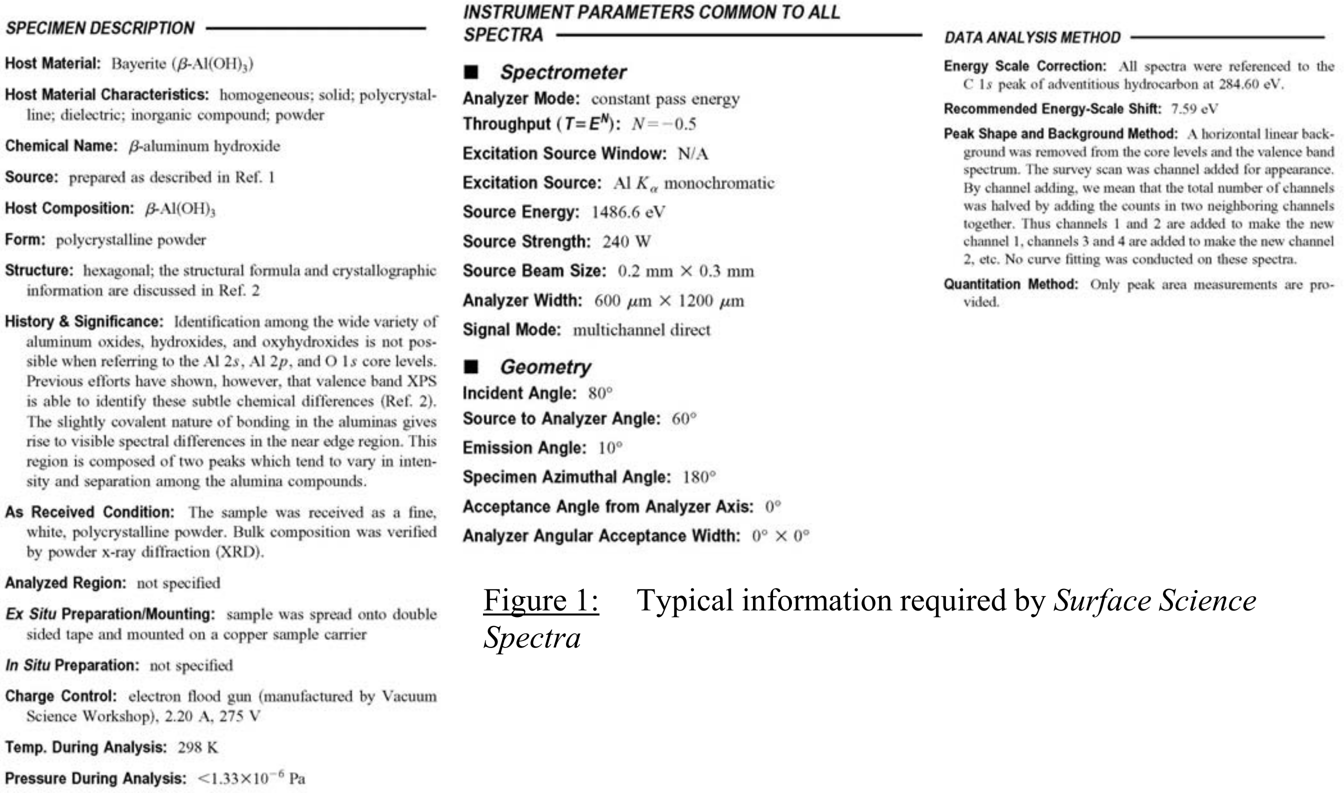
! Sample temperature.

! Take-off angle.

! Record of instrumental data of the sort required by *Surface Science Spectra*.

! The expert system should collect all this data in a VAMAS file. A subsidiary file may be needed to store additional instrumental details.

! Public domain software in a variety of languages should be made available to ensure that the agreed protocols were used in code for expert systems.



SPECIMEN DESCRIPTION

Host Material: Bayerite (β-Al(OH)$_3$)

Host Material Characteristics: homogeneous; solid; polycrystalline; dielectric; inorganic compound; powder

Chemical Name: β-aluminum hydroxide

Source: prepared as described in Ref. 1

Host Composition: β-Al(OH)$_3$

Form: polycrystalline powder

Structure: hexagonal; the structural formula and crystallographic information are discussed in Ref. 2

History & Significance: Identification among the wide variety of aluminum oxides, hydroxides, and oxyhydroxides is not possible when referring to the Al 2*s*, Al 2*p*, and O 1*s* core levels. Previous efforts have shown, however, that valence band XPS is able to identify these subtle chemical differences (Ref. 2). The slightly covalent nature of bonding in the aluminas gives rise to visible spectral differences in the near edge region. This region is composed of two peaks which tend to vary in intensity and separation among the alumina compounds.

As Received Condition: The sample was received as a fine, white, polycrystalline powder. Bulk composition was verified by powder x-ray diffraction (XRD).

Analyzed Region: not specified

***Ex Situ* Preparation/Mounting:** sample was spread onto double sided tape and mounted on a copper sample carrier

***In Situ* Preparation:** not specified

Charge Control: electron flood gun (manufactured by Vacuum Science Workshop), 2.20 A, 275 V

Temp. During Analysis: 298 K

Pressure During Analysis: $<1.33\times10^{-6}$ Pa

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ ***Spectrometer***

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): $N=-0.5$

Excitation Source Window: N/A

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 240 W

Source Beam Size: 0.2 mm × 0.3 mm

Analyzer Width: 600 μm × 1200 μm

Signal Mode: multichannel direct

■ ***Geometry***

Incident Angle: 80°

Source to Analyzer Angle: 60°

Emission Angle: 10°

Specimen Azimuthal Angle: 180°

Acceptance Angle from Analyzer Axis: 0°

Analyzer Angular Acceptance Width: 0° × 0°

DATA ANALYSIS METHOD

Energy Scale Correction: All spectra were referenced to the C 1*s* peak of adventitious hydrocarbon at 284.60 eV.

Recommended Energy-Scale Shift: 7.59 eV

Peak Shape and Background Method: A horizontal linear background was removed from the core levels and the valence band spectrum. The survey scan was channel added for appearance. By channel adding, we mean that the total number of channels was halved by adding the counts in two neighboring channels together. Thus channels 1 and 2 are added to make the new channel 1, channels 3 and 4 are added to make the new channel 2, etc. No curve fitting was conducted on these spectra.

Quantitation Method: Only peak area measurements are provided.

Figure 1: Typical information required by *Surface Science Spectra*

(1) Design of 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).

Data Collection issues.

! FRR may have some advantages for quantification and for Auger spectroscopy.
! The Awizard@ should interrogate the user to ensure that they are using FRR or FAT appropriately with the correct pass energy or retardation ratio and slit settings.
! NPL provides software for the determination of the transmission function of any spectrometer (the software may still be under development?)

Issues related to Data Collection using single and multiple detectors.

The following issues were identified:
! Software issues associated with collecting data in such a way as to ensure that the data is unaffected by poor performance or no performance in one or more channels.
! Expert system needs to check whether the user has set the correct voltage on the channel plates or channeltrons. It may be necessary to set different voltages on different channeltrons in the case of multiple channeltron systems.

Issues related to collecting data that is spatially resolved.

The following issues were identified:
! AWizard@ could assist the user in selecting the best image area size to provide the most unambiguous image.
! Consideration should be given as to the best method for storing images so that they can be downloaded to expert system software. For example JPEG files only allow 256 greylevels and 256^3 colors. JPEG files are a compressed format so some data is lost. Bitmaps are the best format, but occupy a large amount of space.
! VAMAS can store image files, but the image information needs to be in ASCII, which requires an agreed conversion method from a graphics format, and a large amount of storage space.

Auger Features and the Auger Parameter.

The following issues were identified:
! AWizard@ should notify the user of the position and shape in the energy range of likely Auger peaks.
! AWizard@ might notify user as to the possibility that there might be a chemical shift on the Auger peaks, and whether the Auger peaks are likely to experience splitting as a result of final state effects (multiplet splitting).
! AWizard@ should alert the user to the potential value of recording a narrow scan of a Apromising@ Auger region. For example if the user is examining the C1s region the Awizard@ might suggest examining the C_{KLL} Auger region. Another example would be a recommendation to use the appropriate Auger region to obtain an Auger parameter.

Satellite Features.

The following issues were identified:

! AWizard@ should be able to access a library of satellite information associated with particular Ashake-up@ and Ashake-off@ (Ashake-off@ features are much less common and generally much broader than Ashake-up@) features and notify the user of their likely energy. When achromatic radiation is used it is especially important for the AWizard@ to monitor the change in relative intensity of the satellite feature and the main peak as a monitor of potential decomposition. There is no obvious way of distinguishing between Ashake-up@, Ashake-off@ and multiplet splitting.

! In the case of identified decomposition, the Awizard@ would suggest possible decomposition routes, and encourage the user to examine other appropriate regions (e.g. noting a change in metal to oxide ratio).

! AWizard@ should keep a record of the relative area of the satellite and main peak that would prompt the user to include the area of both satellite and main peak in any subsequent quantification.

! The AWizard@ should keep a library of plasmon positions of metals and conductors. It should warn the operator of the likely presence of plasmons, indicating that their presence should not be confused with oxidation, and reporting the level of oxidation by monitoring the O1s and metal intensities in appropriate cases.

! The AWizard@ should indicate possible other potential operator confusion, e.g. between the plasmons in silicon and the S2p and the B1s features.

(2) Regions of binding energy to be scanned.

Region Settings

In narrow scan regions it is important that the appropriate step size be used. The AWizard@ should address the following issues:

! The resolution of the analyzer should be compatible with the linewidth of the photon source and the anticipated FWHM of the level under study.

! The step size should be set so that it is compatible with the anticipated FWHM of the peaks under study in the narrow scan region.

! Such condition generally require the collection of at least 10 points per eV, compatible with time and cost considerations.

Referencing

The following issues should be addressed:

! The instrument must be calibrated.
! Energy referencing of insulators always presents uncertainties, but hydrocarbon with C1s=284.6eV (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.

AWizard@ might suggest:

! Always record C1s.
! Conduct a user interview to get information that will enable the Awizard@ to address the following issues:
  " Identify energy differences between appropriate peaks, e.g. in a metal region note separation between peaks corresponding to chemical shifts (e.g. metal and oxide).
  " Look for possible differential sample charging occurances.
  " Suggest biasing sample to separate out species due to different surface chemistries if appropriate:
    - Biasing can identify the presence of differential sample charging.
    - Biasing can be used to Aseparate@ out different chemical species on the basis of their differences in electrical conductivity. This can be very effective when large bias voltages are applied.
  " In appropriate cases referencing with respect to the Fermi level can be very effective. Unfortunately the Fermi level is not always easily identified.

Auger Parameter

The AWizard@ should make the following recommendations:

! Record an appropriate Auger peak and generate the Auger parameters. This process requires little extra time and frequently leads to a large information gain.
! Expert system should generate the chart, as well as having a database of Auger Parameter charts.

What core regions might be interesting?

AWizard@ should recommend that the user always run a reasonable quality survey (wide or overall) scan and the following regions:
! C1s.
! O1s.
! Appropriate core level lines. The most cost effective approach is to use the most intense core line.

" The most intense line may have problems, because there may be interference with other regions or it may be broad with ambiguous satellite features.

" The AWizard@ might identify the most intense peak, point out potential problems with this region, and suggest alternatives.

" The AWizard@ might prioritize various regions that might be fruitful with a time estimate.

! In the case of core lines with spin-orbit split components it is important to measure both lines. This splitting can contain chemical information.

! Record different core level lines for the same element, this can give one non-destructive depth profiling information.

! Single crystal samples present extra opportunities. These include:

" Diffraction effects that lead to variations in the peak intensity with take off angle. Experiments that vary both the take off angle and the sample orientation can be especially valuable.

" Intensity variations in the valence band for single samples can be used to identify orbital type.

Valence Band Studies

The valence band contains valuable information. The AWizard@ should address the following issues:

! If a Polymer:

" AWizard@ questions the operator as to likely candidates for polymer or polymers in the spectrum. The AWizard@ checks the appropriate data base to see if the spectra are likely to be different. In the case of mixed polymers the AWizard@ could evaluate if a difference is likely to be seen.

" AWizard@ provides recommendations as to instrument use (e.g. could one obtain any useful information with an achromatic source B based upon resolution and sample degradation B e.g. a Adegradation index@).

! If an inorganic compound or a metal:

" AWizard@ questions the operator as to likely candidates for surface species and compares with a limited (but hopefully growing) database, and makes recommendations.

" AWizard@ reminds users that a calculation is probably necessary. In the future a Awizard@ could guide the user in conducting a calculation.

" AWizard@ could recommend whether the contamination level makes obtaining UPS data reasonable or not (I.e. whether the spectrum would be dominated by hydrocarbon or not), and could make recommendations for the subtraction of hydrocarbon features.

" Degradation issues are less significant in the valence band region because the region probes more deeply into the sample. However valence band spectra require much long acquisition times.

" Knowledge of the transmission function is especially important for UPS because of the large change in transmission function over the narrow scan region for low kinetic energy electrons.

3) Number of counts (time) required for experimental objective(s).

! The AWizard@ should contain the equations in the following papers:
  " Definition of S/N: M.F. Koenig and J.T. Grant, *Surf. Interface Anal.*, **13**, 63 (1988).
  " Strategy for best practice: K. Harrison and L.B. Hazell, *Surf. Interface Anal.*, **18**, 368 (1992). Hazell strategy requires a wide scan or some other primary knowledge to be obtained first in order to determine the dwell times to be used for the subsequent narrow scans.
! The AWizard@ will then suggest the appropriate energy window, number of data points, the choice of FRR or FAT mode, damage considerations (see earlier recommendations) and collection time needed to appropriately exploit the above suggestions.
! The AWizard@ would recommend that additional data be collected at the high and low energy background positions, and this additional information be added to the data. Users will be recommended to report the different collection times in different parts of the spectrum.
! The AWizard@ would question the user regarding any situation where the sample is ion-etched. This information may require additional experimental data from overall scans during the etch process. The AWizard@ would then use the extensive data bases to recommend the appropriate energy window based upon the anticipated products of the etching process.
! Changing surface conditions due to damage or contamination should be monitored by quick overview (survey) spectra which would allow the AWizard@ to alert the user about decomposition. It is recognized that some instruments will not allow quick overview (survey) spectra. The user would need to determine whether to Aswitch on@ this facility, and determine the statistics necessary to reasonably make this determination.

4). Avoidance of Potential Problems.

Overlapping Peaks from Different Elements

There are various unfortunate overlaps. Look for example for overlaps between:

! Sr3d and P2p.
! Sb3d and O1s.
! V2p and O1s.
! Cu3p and Al2p.
! Na Auger and Zn Auger.
! K2p and C1s.
! A peak from electron sources found in instruments such as mass spectrometers attached to the vacuum system.

AWizard@ will remind users of the advantages of using alternative photon sources to address some of these problems.

AWizard@ will search database for potential overlaps. Database needs the peak positions and peak widths and lineshapes to be effective in this role. The Database must include all possible peaks including Auger features and very low intensity features.

Need to make measurements for elemental peaks before onset of specimen degradation, etc.

- AWizard@ has already been seen to monitor for the presence of degradation. If degradation were found the AWizard@ would be Atuned@ to hardware system to exploit possible features associated with issues such as reducing X-ray flux, distance of X-ray gun from sample, adjusting focus, moving sample, placing a mask on the sample that reduces the area of the sample exposed to the X-rays, cooling the sample, etc. (Hardware issue: X-ray guns that have a water-cooled cap can substantially reduce sample damage).
- AWizard@ might suggest that the user using sample cooling when it identifies decomposition. Pressure monitoring via a quadrupole might warn the user about ice formation when the partial pressure of water is high. AWizard@ would evaluate the likely formation of ice for different surfaces, for example a low thermal conductivity polymer would be less at risk than a high conductivity polymer.
- AWizard@ might warn the user about the possible formation of ice on the sample surface, and examine the collected data to see if it corresponded to ice.
- Many hardware issues. Need to prevent decomposition, examine liquids, and examining frozen gases.
- AWizard@ might train the user in hardware aspects of cooling. An appropriate link to the manufacturer recommended approach would be appropriate.
- AWizard@ should ensure that all data is collected and stored in a temporary file to allow the user to access any data element within a given time period before the file is erased (hard disk space is very cheap).
- Issues:
  - What is the decomposition route, heat from the X-ray gun or photon flux?
  - How important is the choice of substrate B will one substrate lead to the generation of more secondary electrons which might impact sample decomposition.
  - Potential Aflood gun@ damage can occur. The AWizard@ might use a Adamage database@ to evaluate this potential problem. There are enormous variations in flood gun and instrument design that can impact this issue. The frank and complete disclosure of data from the manufacturers would be very helpful here.

- **Smoothing may be necessary**
  - Curve Fitting should be conducted on unsmoothed data.
  - The cosmetic improvements provided by smoothing can be helpful in some cases, and the AWizard@ should advise the user as to the best course of action and the appropriate choice of smoothing conditions, e.g.
    - Comparison of valence band spectra with spectra predicted by calculations (Aguide to the eye@).

- Display of data collected for a short time period before the onset of decomposition, as a means of assisting the user in identification of the main spectral features (another Aguide to the eye@).
- Data can be usefully treated by smoothing before the data is deconvoluted or differentiated (especially true of the second derivative). The AWizard@ should advise the user as to the best choice of smoothing conditions before such treatment.

" The AWizard@ will display a number of Aoptimized@ results for smoothing and derivative spectra using a number of different methods for conducting these processes. This provides the user the opportunity to select the best choice.

" The AWizard@ will warn the user of any potential noise spikes present in the data, and to warn the user not to attempt to oversmooth the data in an attempt to remove noise spikes. The AWizard@ will offer the user the option of removing noise spikes.

The AWizard@ might determine whether the data falls outside a specified range, for example by taking three data samples for each point (i.e. 30ms count repeated 3 times) or investigating differences from one spectral range collection to another. The choice of which method to use will depend upon whether decomposition is suspected.

5) Analysis of Narrow Scan Data

Comparison with Wide-Scan Data

! Errors when intensity measurements are made (area of peak used will be in error when wide-scan data used). Wide-scan group C recommends 0.4 eV steps and a 2eV analyzer resolution (this may present problems for some instruments), which will minimize the errors involved.

! Wide-scan data may assist in the identification of satellite features, so allowing appropriate narrow-scan regions to be chosen.

Presentation of Spectra for Subtraction of Backgrounds

! Spectra need to be collected over a sufficiently large energy range to allow the appropriate background to be subtracted, and the appropriate intrinsic and extrinsic satellites to be included. The AWizard@ would recommend to the user the appropriate range to choose based upon its stored databases, and a knowledge of spectral energy shifts associated with charging or biasing.

! It is essential that the user indicate that quantification data is based upon certain assumptions that may assume that the sample is homogeneous over the sampling depth, or contains a particular topography (e.g. a uniform overlayer).

! When achromatic data is used the spectral energy range needs to be large enough to include the main $K\alpha_3\alpha_4$ X-ray satellites.

Interactive Curve-Fitting or Peak Shape Analysis

! The output of the fitting process 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 (the difference between the experimental data and the fitted profile).

! Curve Fitting is only meaningful if it is conducted in a chemically meaningful way.

! Curve fitting requires appropriate appreciation of the chemical issues involved, needing an appropriately educated expert system. Thus the expert system should contain an updateable data base that contains knowledge of the growing understanding of the factors that give rise to different chemical shifts and other spectral features.

! The AWizard@ should alert the user to the following points before curve fitting:

" It is important to have sufficiently high quality data to obtain the most reliable curve fitting (cost considerations are important). The AWizard@ will indicate a suggested Asufficient@ value.

" The user must decide on the number of peaks to be used, the fitting function to be used, and the parameters for each chemical species.

" The choice of the number of components can be assisted by (the AWizard@ will alert the user about the likely time required for these procedures):

- Generating a second derivative spectrum and using this to indicate approximate numbers of peaks and their peak positions.
- Deconvoluting the spectrum to determine possible component features.
- N.B. The Wizard should point out that curve fitting is different from deconvolution.
- Conducting factor analysis on the data.
- Pattern recognition may help.
- The use of spectral subtraction or spectral addition may be helpful.

! The AWizard@ should alert the user to the following points:

" The choice of background can make a substantial difference in the relative areas of peaks associated with different chemical species. The iterative Shirley background often gives better fits over a narrow energy range. It should be noted that the Shirley model has a number of deficiencies, especially when applied to non-conducting materials.

" The AWizard@ would have an updateable database of references to background models.

" The choice of the high and low energy values for the background can have a major impact on the likelihood of convergence in the fitting process.

" The choice of fitting function can have a major impact on the likelihood of convergence since fitting functions with extensive tails will impact the convergence behavior in narrow energy scans.

" Appropriate curve fitting involves using different fitting functions for different chemical species involved in the fit.

" Once the curve fitting process has been completed, the AWizard@ should assist the user in determining the extent to which the fit is chemically meaningful, consistent with the limitations imposed by the collected data (e.g. step size and energy resolution), and based upon sound physical principles.

  " The AWizard@ should remind the user that there is no unique fit possible, and that the user should report the choice of function and the rationale for the other choices made in any publication.

  " Appropriate statistical analysis can be used to reduce the number of eligible fitting possibilities. The AWizard@ may suggest to the user a more appropriate set of experimental conditions on rerunning the spectrum (which it should have picked up in the first place Bchallenge to the AWizard@ creators.

  " A successful curve fitting approach which provides a powerful test of the fitting process is to fit a series of spectra where the relative amounts of surface chemical species change. In this series of spectra it is helpful if some species are present in high concentration so that their energy position and shape can be determined.

  " The use of reference spectra is essential in meaningful curve fitting. For example in a system consisting of a metal and an oxide, the fitting of the pure metal and the pure oxide allows the user to optimize the fitting function and its parameters for these species.

! Key Recommendation: The AWizard@ really needs to be a AGood Fairy@ and this is the huge challenge to the AWizard@ creator.

! Good luck in implementing these recommendations from Group D!