

Report of the International XAFS Society Standards and Criteria Committee

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The Standards and Criteria Committee of the IXS presently consists of four subgroups, Beamlines, Data Analysis, Error Assessment and Reporting, and XMCD. The role of each subgroup and the present membership can be found on the IXS web site (<http://ixs.csrrri.iit.edu/>). The committee met in Seattle on July 31 and August 1, 1997 to plan its agenda and to begin its work focusing, in the short term, on a report to the XAFS X Conference in Chicago. It met again in August 1998 in Chicago but did not finalize its report. A third meeting was held at LURE in July 1999 to further discuss both the committee report and the error reporting recommendations as well as to plan the activities prior to the XAFS XI Conference in Japan. It met again in July 2000 to finalize reports for the conference and to plan for the future. This document represents a progress report of the activities for each subgroup of its activities for the past few years. A specific error reporting recommendation will be presented separately.

1. Beamline Subgroup

Experimental techniques involve a variety of issues. In this report, we have separated these issues into three main areas: user controlled issues, data collection modes and facility hardware. User controlled issues include sample preparation techniques, harmonic monitoring and control, detector checkout at the start of the measurement, energy calibration, and characterization of the energy resolution. The choice of data collection mode requires a detailed understanding of their strengths and weaknesses. Facility hardware questions are often not under the user control, and improvements can only come through the EXAFS community clearly making its wants and needs known to machine and beam line operators. The discussions in this report are mainly applicable to crystal monochromator systems that collect data in air or after an exit window but are applicable to some softer x-ray energy systems. The purpose of this report is to identify and discuss some of the major experimental issues. Later this subgroup will develop and undertake performance tests at XAS facilities around the world.

1.1. User Controlled Parameters

Noise levels in EXAFS measurements are usually *not* limited by photon statistics. Instead, the overall uncertainty is usually dominated by a number of systematic measurement errors, many of which can be minimized on individual experiments. The purpose of this section is to identify the most obvious of these and suggest some possible solutions.

First, sample preparation is a critical issue that can only be controlled by the user. Transmission samples need to be uniform [Goulon et al., J. Phys. (Paris) **43**, 539 (1983);

Ottaviano et al., Phys. Rev. **B49**, 11749 (1994)]. It is recommended that for concentrated materials $\Delta\mu x \leq 1$, or for materials where the element of interest is more dilute or there is a heavy matrix the total absorption above the edge, $\mu x \leq 2$. Absorbencies higher than these will give diminished amplitudes, unless there are really are *no* harmonics in the beam or pinholes in your sample eg mirrors rejecting harmonics rather than just detuning the monochromator. Even then it is recommended that $\Delta\mu x \leq 1.5$. In general, sample thickness should be optimized to minimize systematic errors, *not* to maximize photon statistics. Only when the incident flux is very low (i.e. high energy on some beamlines) should thicker samples more optimized for counting statistics be used, $\Delta\mu x \leq 2.6$. When making these estimates, it is important to consider the contribution to the total absorption from windows on sample holders, and cryostats or furnaces. One should be careful that all the X-rays hit the sample and the sample cell or holder does not cut any part of the beam or else “noisy” data and glitches may result. This is especially true when using sample stages (e.g. cryostats) which might be difficult to see inside. Be aware of thin polymer windows that might bow under pressure. If this is the window to a solution cell then the curvature will give a variance in thickness across the beam. Similar problems can result if there is a bubble in your solution.

When powder samples are measured, particle size should be as small as possible. This should be much smaller than one x-ray absorption length [Lu and Stern, Nucl. Instrum. Meth. **212**, 475 (1983)]. Note diluting sample powders in a low Z matrix is not a substitute for producing small particle size. Also, stacking more layers of a non-uniform sample changes the average thickness, but not the distortions due to sample non-uniformity. If possible, representative samples should be measured at two different thickness, and the amplitudes of the EXAFS compared. This is a good overall test for a variety of thickness related effects, including sample non-uniformity, harmonic content of the beam, and leakage through or around the sample.

Signal drifts can be an important systematic error. These can be due to drift of electronic components, thermal affects on beamline optics, or for ionization chambers operated at atmospheric pressure from changes in the atmospheric pressure. Diagnosing these typically requires some degree of analysis while taking the data.

For fluorescence, the sample must be measured in the “thin-concentrated” or “thick-dilute” limits. Where possible, electron yield should be used instead of fluorescence for “thick-concentrated” samples. Errors caused by departure from these limits should be estimated. Comparisons between samples measured in transmission and those measured by fluorescence or other indirect techniques require correction of EXAFS amplitudes to account for the energy dependence of the detector response. Similar corrections are needed when comparing indirect data with theory. Correction routines are built into most analysis packages.

Harmonics passing the x-ray monochromator should be evaluated *quantitatively*, and the methodology used to eliminate them should be reported. If possible a harmonic detector should be operated throughout the data collection. Harmonics may be minimized by detuning the monochromator, or by using a total external reflection mirror. The use of a mirror is generally the best choice, but especially so if the crystal is bent for sagittal focusing as just detuning the mono may allow significant harmonics to pass. Monochromator crystals may also be chosen to minimize the harmonic content of the

beam by using reflections for which the second harmonic is forbidden. The effect of residual harmonics can also be minimized by the use of thin samples and x-ray detectors that do not strongly absorb the harmonic.

Detectors must be characterized as completely as possible. Running $I - V$ characterization can verify that the ion chambers are operating in the linear range, by determining the saturation region where I is independent of V . Typically the chamber should be operated at more than twice the saturation voltage, but it is good practice to use as large a voltage as possible [Pettifer et al., *J. Syn. Rad.* **6**, 217 (1999)]. Placing attenuators in front of I_0 can check the linearity of I/I_0 . A simple method is to scan through the edge of a calibration foil placed in front of I_0 . The residual edge observed in the ratio is a quantitative measure of the linearity. The x-ray beam must be defined by slits in *front* of the I_0 detector, and, except for attenuation by the sample, the same beam must be measured in both detectors. To insure accurate digitization, voltage-to-frequency converters should be operated near the center of their range. Many amplifiers and voltage-to-frequency converters suffer from extra non-linearity when operated near zero voltage. It is often desirable to operate with a finite (50–100 mV) offset voltage to avoid this region. In this case the offset value should be determined with the beam off, and subtracted from the measured signal. Most voltage-to-frequency converters are unipolar, and do not average the signal properly if it is crossing zero. For this reason the offset voltage should always be set greater than any noise fluctuations.

Energy calibration can be checked by measuring standard absorption edges, from monochromator glitches, or by using Bragg reflection calibrators [Pettifer and Hermes, *J. Appl. Cryst.* **18**, 404 (1985)]. Recently the absolute calibration of many common metal edges has been reported [Kraft et al., *Rev. Sci. Instrum.* **67**, 681 (1996)]. These can be used to put the data on an absolute scale. It must be remembered, however, that all mechanical systems can have some errors, and the further the energy is scanned from the calibration point the more likely are errors. Measuring known absorption features can be used to check energy resolution. Since there are no universal standards for energy resolution or calibration, it is crucial to state how calibration and resolution were determined. It is recommended that the work of Kraft et al. be continued to develop a more complete catalog of standard edges with well-characterized absorption features that can be used to check both energy resolution and calibration.

1.2. Data Collection Modes

Depending on the nature of the samples to be measured there are several methods for collecting data:

1.2.1. Absorption

Direct transmission measurements can be carried out using two schemes: scanning and energy dispersive. In the scanning method the data is collected step-by-step at individual energies. The traditional method halts the monochromator at each energy point. The quick-XAFS (QEXAFS) [Frahm, *Nucl. Instrum. Meth. Phys. Res.* **A270**, 578 (1988)] method continuously drives the monochromator, and collects the individual

energy points “on the fly”. This has the advantage of significantly reducing the scanning overhead, and thus the scan time, but requires a stable monochromator that does not vibrate the crystals during scanning and data acquisition needs to be fast to avoid loss of energy resolution at the edge.

The energy dispersive mode uses a bent crystal and a position sensitive detector to collect the entire spectrum in a single time interval. The crystal is bent such that a range of energies is focused to a single point at which the sample is placed. After this focus the individual energies diverge, and can be individually detected on a position sensitive detector. Because of the limitation of Bragg or Laue reflection the scanning and dispersive methods record the same total flux of photons for the same total scan time (assuming the beamline collects the same solid angle from the source in both cases). Because there are no moving parts the dispersive method can have some stability and reproducibility advantages, but it can only be applied to transmission measurements, and requires a specialized beamline setup.

1.2.2. Radiative decay

The absorption process results in the creation of a hole in a core shell. The excited atom and the system will relax in either radiative or non-radiative ways. For x-ray fluorescence emission that leaves the excited atom in a lower energy excited state, the quantum yield is assumed to be energy independent, making the intensity of the *fluorescence signal* proportional to the primary absorption process. This may also be true for optical emission, especially away from the near edge region. However the optical case is especially sensitive to light scattering from surface defects or powder grains, and special care is needed in sample preparation.

1.2.3. Non-radiative decay

Electron yield is dominated by two-electron process, one of which, the Auger electron is ejected from the excited atom. In Auger spectroscopy, the electron detector is tuned to the energy of the Auger electron, which is specific to the probe atom. Thus, there is no basic difference, in principle, in detecting this process or the fluorescence yield. The choice of one scheme with respect to the other has to take into account: (1) the atomic number (Z). Low Z atoms decay preferentially through the Auger electron process; (2) the ability to collect electrons emitted in a large solid angle; (3) the difficulty in collecting electrons with good energy selectivity without using a high vacuum detector; (4) the large probability that the Auger electron will undergo inelastic collisions. Because of the relatively short inelastic mean free path of the ejected electron (5–100 Å), Auger detection provides a signal specific to the near surface region and for most cases Auger yield is restricted to investigations that require UHV conditions.

If the energy band pass of the detector is opened partially (partial yield) or opened totally (total yield, TEY) the signal collected then includes Auger electrons which have undergone inelastic collisions. In addition the total yield spectrum will include contributions from secondary electrons and other effects, but in the gaseous environments normally employed for TEY the Auger electrons dominate the signal. For electrons with

energy greater than the gas ionization potential, multiple electron ion pairs are generated thus providing an internal gain. Since this gain increases with the electron energy, the high energy electrons are preferentially detected. In this case the escape depth of the Auger electrons determines the surface sensitivity, which is typically 100–2000 Å, although it can be larger in some situations. As soon as this depth is much smaller than the absorption length of the exciting X-ray, the total yield intensity is proportional to primary core-hole creation probability (i.e. the absorption). All the methods using decay channels are incompatible with dispersive XAFS methods.

We now consider the special characteristics of the common detection techniques: transmission, fluorescence, and electron yield.

1.2.4. Transmission

Issues pertaining to transmission measurements in the standard step-by-step mode were considered in the section on user controlled issues. Most of the same considerations apply to dispersive mode transmission measurements. There are, however, some special characteristics of dispersive measurements that deserve mention.

1) All energies are collected at once, hence it offers the possibility of the fastest time resolved measurements. Current beamlines can collect data in a msec or better, but sample dilution and counting statistics often require a longer time. Most interesting samples require of the order of 100 msec for good statistics.

2) The quality of the data can be affected by temporal and spatial fluctuation of the source, so it is important to collect I_0 and I_t as close in time as possible. However, the lack of mechanical movement during the data collection yields a high stability of the energy scale.

3) The dispersive method automatically provides a small focus (typically sub-millimeter) which is advantageous for high pressure experiments, however, the homogeneity of the energy distribution within the focus spot is not perfect. Recent developments of 4-point benders have improved this, but there is still a high sensitivity to sample inhomogeneity and powdered samples require great care in preparation. Recent improvements in optics and sources (i.e. undulators at third generation sources) have made the attainment of sub-millimeter beams routine at standard XAFS beamlines as well.

1.2.5. Fluorescence

It is now well known that measuring fluorescence excitation spectra is more efficient than conventional transmission experiments:

- a) for dilute systems,
- b) when that sample is too absorbing, a situation which often prevails for soft x-ray experiments (e.g. below 5 keV), and,
- c) when it is not possible to prepare samples with enough homogeneity for carrying out transmission experiments.

For points b and c, electron yield detection should be considered for samples that are not too dilute.

One should keep in mind that even though x-ray fluorescence excitation spectra have basically the same structural content as transmission spectra, the relative amplitudes of the observed structures might be different. There are at least two physical reasons:

a) For a thick sample and considering the simplified (and often used) case where the beam enters and the fluorescence exits the sample at 45° the measured ratio I_f/I_0 is proportional to $\mu(E)/(\mu_T(E) + \mu_T(E_f))$ where μ is the absorption due to the element of interest and $\mu_T = \mu + \mu_B$ is the total absorption. For the typical fluorescence case on a dilute sample, $\mu \ll \mu_B$, and the signal is strictly proportional to the fluorescence. If the sample is concentrated then the $\mu(E)$ terms in the numerator and denominator tend to cancel, reducing the measured amplitude of the oscillation. This is termed self-absorption. This case will require correction which is generally more complicated than the above since the finite solid angle of the detector must be averaged over [Tan et al., Rev. Sci. Instrum. **60**, 1021 (1988)]. In addition the non-linearity leads to deterioration of the counting statistics which then gives considerably worse signal to noise ratios, and so it is strongly recommended that the data is collected in the linear regime.

b) As mentioned above, the quantum yield of the fluorescence process is usually regarded as being constant over the whole energy range of the XAFS spectra. However, there is no reason to believe that this is correct in the pre-edge region, especially in the case of XANES spectra recorded in the soft x-ray energy range. One has, therefore, to be extremely careful when comparing XANES spectra recorded in different modes at low energy.

From the experimental point of view there are a number of difficulties that have to be overcome:

a) Detectors should cover a large solid angle and have high count-rate capabilities. Because scattering is suppressed by a polarization factor, it is advantageous to orient the detector along the polarization direction. Generally the solid angle should be as large as possible, although the increase in scattering away from the polarization direction may make restriction of the solid angle desirable for some cases.

b) Elastic and inelastic scattering contaminating the fluorescence signal should be reduced as much as possible. At present, discrimination between fluorescence and scattered/diffracted photons can be obtained by using $Z - 1$, $Z - 2$ filters, in limited ranges, or by using a large array of energy dispersive solid state detectors as described below.

Solid State Detectors

Solid state detectors are now in regular use for fluorescence measurements on most beamlines specializing in XAS and it is worth considering them separately. Whether consisting of a single element or a large array of elements, the operating principles of SSD's are largely the same.

A semiconductor pn junction is depleted of carriers by an applied bias voltage (effectively a reverse biased diode). When a fluorescence photon is absorbed in the diode, a number of electrons proportional to the photon energy and inversely proportional to the bandgap are excited into the conduction bands. Electrons flow towards the anodes, holes towards the cathodes, under the influence of the bias field. Charge sensitive preamplifiers on either the anodes or cathodes amplify the collected charge to produce a set of voltage steps, the height of which are again proportional to the photon energy. By

further amplifying these steps with shaping amplifiers, pseudo-gaussian shaped pulses can be produced which are suitable for pulse height analysis to determine the energy of each incident photon.

The immediate advantage of photon counting with energy sensitivity is the ability to ignore elastic scatter or signal from matrix atoms which would normally contribute to a background which degrades the signal to noise ratio. There are disadvantages to using SSD's, the primary of which is the limitation in count rate imposed by the shaping times in the amplifier sections. Whereas an ion chamber such as a Stern-Heald or Lytle detector can easily deal with 10^8 to 10^{10} photons/second, but with no energy resolution, the early generation solid state detectors were only capable of 10^4 counts/second before saturating. The latest solid state detectors are capable of up to 10^5 or even a few 10^5 photons/second. This is the motivation for the development of large parallel arrays of SSD's: to improve the total count rate capability and solid angle covered. Solid state detectors have some other disadvantages relative to fluorescence ion chamber detectors, including increased complexity in the setup of the experiment and some inherent fragility. However, state-of-the-art SSD's make use of user-friendly software to minimize the time and effort overhead demanded of the experimenter. With reasonable care to maintain vacuum and cold temperatures, SSD's can be kept operational for years. Finally, it should not be forgotten that scintillators do offer counting rates $>10^6$ photons/sec and also afford some energy resolution, sufficient to reject harmonics and because of their higher counting rates can offer better data quality than SSD's for moderate dilutions.

For application in a given experiment, the user needs to keep a few key concepts of SSD's in mind:

a) The SSD diode must be able to stop the desired photons, i.e. have an atomic Z and thickness that correspond to at least two absorption lengths.

b) The count rate must be checked throughout the EXAFS range to ensure that it does not exceed a tolerable limit. When rates are too high, pulses tend to "pile-up" on top of each other and migrate out of the pulse height analyzer windows. This leads to nonlinearities in the data.

c) There is always a tradeoff between shaping time and resolution. The detector should be adjusted to the shortest shaping time that gives resolution adequate to separate the elastic scatter at the absorption edge from the desired fluorescence.

d) SSD's are susceptible to noise pickup as a result of their large amplifier gains. Cable runs should be kept as short as possible and avoid obvious interference sources such as computers and monitors.

e) All SSD's suffer to some extent from "dead time", i.e. there is a finite probability of undercounting pulses due to insufficient time separation between their arrivals. In a graph of number of photons counted versus rate of photons arriving, there is thus a deviation from the ideal: a linear response with a slope of 1. The most precise measurements with SSD's therefore make use of a dead time correction curve that accounts for this effect in a statistical fashion. This can reduce some glitches. If dead time corrections are not used particular care is required in the XANES region where the white line and other large features are most sensitive to dead-time effects, though most researchers find that in EXAFS it results only in a small change in the determined Debye-Waller factor.

1.2.6. Electron yield

In the past electron yield techniques were used mainly in SEXAFS experiments where the high surface sensitivity is a distinct advantage. Total electron yield techniques also offer some distinct advantages for bulk samples. In total electron yield the sample current is monitored, either by collecting it on an appropriately biased electrode, or by biasing the sample and measuring its drain current to ground (i.e. using the sample chamber as an electrode). Generally the best data is collected either when the sample is biased negatively or the counter-electrode positively and current collected from the sample in both cases. This is thought to be due to the repulsion and hence rejection of background electrons at the sample. The gas should be insensitive to emitted fluorescence photons and for bulk samples a low Z fill gas (He or H₂) is generally used as a detecting gas, although other gases can be used. TEY is surface sensitive, but not to the extent that thin (20–30 Å) native oxides are a problem. Heavy oxidation or other surface layers may be a problem. Some advantages and disadvantages are listed:

a) Advantages:

Minimum sample preparation for samples which do not have thick native oxides or other surface layers. Thickness effect problems are minimized (although not eliminated) — can measure near edge resonances accurately. Use of a conversion gas provides high signal levels (typically 100× vacuum detection methods). The technique samples the near surface region. Instrumentation is simple and inexpensive, and can be adapted to a variety of sample configurations, including the reflection technique or in the gas phase. The effect of diffraction glitches from single crystal samples is reduced.

b) Disadvantages:

The detailed physics is not yet well understood, but it is sensitive to the surface, e. g., Cu₂O may easily be identified on the surface of Cu; nonconductive samples need careful preparation if charging effects are to be avoided. The samples may be made conducting by placing on a conductive substrate (Al foil, carbon tape, or conducting grid), but the appropriate choice of conversion gas can also avoid charging. The sampling depth is the electron escape depth, therefore, it may be of limited use for dilute samples or wet samples unless the wet layers are very thin. A concise review of the theory, advantages, disadvantages and practical issues is given by Schroeder et al., Chapter 1 in: *Spectroscopy for Surface Science (Advances in Spectroscopy Vol. 26, Wiley & Sons, Chichester UK, 1998)*.

1.3. Facility Hardware

Hardware related questions are less under the control of the users, but can be addressed by the operators of EXAFS beam lines. The most common problem is that of monochromator glitches. The effect of these can be minimized by linearizing the detection system, and by careful control of crystal alignment, but they are likely to always be a problem for dilute samples. For the users it is important to catalog the glitches from a particular crystal set so that the appropriate set can be chosen for an experiment.

In many cases glitches are a good index of sample preparation and harmonic rejection. When the detection system is linear and the ratio of harmonics is low enough, apparent

glitches in absorption reflect the non-uniformity of the sample or incorrect sample alignment (i.e. some of the beam is blocked by the sample holder). A simple test is useful for characterizing the situation. Measure the XAFS of aluminum foil (or any other uniform material) with a similar absorption to the sample. If glitches are not observed, then sample uniformity or alignment should be suspected. If the glitches are observed, but become smaller as the sample is made thinner, then harmonics are the likely cause.

Many of the issues raised in the section on user controlled parameters require equipment in addition to the two ion chamber absorption setup. Instead of each group supplying such equipment, it makes more sense for the facility to provide it. This includes detectors and electronics for a third energy calibration or harmonic detection channel, Bragg reflecting energy calibration and polarization detectors, fluorescence detectors, and dewars for liquid nitrogen temperature work. A third ion chamber, with a foil or reference sample between the 2nd and 3rd ion chambers, gives an energy calibration for each dataset.

In the future hardware improvement may still be important in improving the quality of data. We believe beam noise is still contributing to the overall signal to noise of the spectra. On-line position monitoring is extremely important in assessing and controlling this problem. Possible improvement in optics which are now being incorporated into some beamlines include harmonic rejection mirrors and active beam stabilization by moving an optical component such as a mirror or monochromator crystal. Care has to be taken in such a scheme that some other parameter such as harmonic content is not varied in an attempt to stabilize the beam.

For characterization of data, it is important that there be on-line data analysis capability. Data should be analyzed at least to the stage of the Fourier transform to assess the data noise, background variations, amplitude variations from thickness effects, and the seriousness of monochromator glitches. While the facility should provide these capabilities, the user should also consider bringing their own computer loaded with analysis software with which they are familiar, or setting up network accessible analysis programs. For this case the beamline operators should facilitate network connections to allow on-line data transfer.

Local user groups have suggested many of these ideas to the facilities over the years, and progress has been made in many cases. It is safe to conclude, however, that improvements are still possible at all facilities.

2. Data Analysis Subgroup

The task of the Data Analysis Subgroup is to develop and recommend standards for XAFS analysis. Previous incarnations of this subgroup have concentrated on defining the basic principles that XAFS data analysis methods should follow, and on recommending standards for presenting the results of XAFS analysis in scientific articles. Those recommendations have been published, in the XAFS V and XAFS VI conference proceedings.

The present committee has chosen to concentrate on evaluating the implementa-

tion of XAFS analysis methods in computer software. The following agenda for the subcommittee was adopted at the IXS meeting in Seattle in 1998:

- a) Create and maintain a list of available XAFS analysis software.
- b) Initiate and report on studies to evaluate XAFS analysis software.
- c) Develop a searchable web-based archive of information about XAFS analysis, analysis software, and previous IXS reports.

2.1. Catalog of XAFS Analysis Programs

An initial survey of the XAFS community was performed to determine what analysis programs are currently in use. A short letter was sent via e-mail to the XAFS-IX Conference, SSRL and NSLS XAFS Users mailing lists. The letter asked which XAFS analysis software the recipient used, and the name of the author, if known. Out of 685 messages sent, 190 replies were received listing 63 authors of 25 separate XAFS analysis programs, not counting custom software used only by the respondent.

Based on this information, a long questionnaire for gathering detailed information on the features and availability of these analysis programs was mailed to each of the authors named in the first survey. Replies to the author's questionnaire were merged into a database, and a searchable web site to make this information available to the community was prepared.

The catalog of XAFS Analysis Programs is accessible through the IXS web site. The URL is:

http://ixs.iit.edu/catalog/XAFS_Programs

The catalog currently holds information on 36 computer programs for XAFS data reduction, analysis and theoretical XAFS calculations. These are:

ATOMS	AUTOBK	AUTOFIT	BAN
CDXAS	CERIUS2	EXAFS	EDA
EX.TR.A	EXAFIT	EXAFS/FITEX	EXAFS pour le Mac
EXAFSPAK	EXBACK	EXBROOK	EXCALIB
EXCURVE	FEFF	FEFFIT	FUSE
G4XANES	GNXAS	LASE	MacXAFS
REDUCE	REX	REX2	SEDEM
TT-MULTIPLETS	VIPER	WinXAS	XAFS
XAID	XANADU	XDAP	XFIT

Information about each program is divided into fields, such as title, author, supported platforms, special fitting features, etc., and the catalog search feature gives several ways to access this information. The web interface provides a means for XAFS users to learn about different XAFS analysis options, and for software authors to compare the features of their codes with others.

No judgement has been made about the relative merits of the software in the catalog. We note that some of the programs are targeted at specialized techniques, e.g., energy dispersive XAFS, and will require special testing criteria. We also note that there are very large performance differences among the programs in the catalog. Some of them

provide little more by way of analysis than background removal, step normalization, and Fourier transform, while others provide sophisticated physical model-building capabilities and parameterized fitting with error analysis.

2.2. Data Analysis Software Evaluation

Based on the experience of the International Union of Crystallographers in evaluating analysis software, we expect that the evaluation and comparison of XAFS analysis software will be an ongoing process. The results of the first comparison tests of programs in the Software catalog, using representative XAFS data, will be reported at XAFS XI in 2000.

3. Error Assessment and Reporting Subgroup

The 1997 Seattle meeting of the IXS S&C identified the following areas as topics for future work of the Error Group:

- a) Development of standardized error-reporting procedures and minimum reporting requirements.
- b) Procedures for applying significance tests (a.k.a. Joyner or F-tests) to EXAFS data.
- c) Identification of sources of error: experimental, theoretical, and data processing.
- d) Determination of the parent distribution of experimental errors in EXAFS data through a round robin test of various EXAFS beamlines with a standardized sample set.
- e) Modeling of the effect of errors on the data analysis process. This includes Monte-Carlo modeling, propagation of errors through the background-subtraction and Fourier-filtering procedures, serial correlations, interpolation-induced correlations, etc.
- f) Identification of figures of merit that can be used by the Experimental Methods subgroup to develop beamline performance tests.

Of these, (a) and (b) were considered relatively short-term. Areas (1–5) are described in some detail below. The discussion in area (f) was limited, and no specific plan for future work was adopted.

3.1. Standardized Error Reporting Procedures

Ideally the estimation of errors should include both statistical errors and systematic experimental and data processing corrections. However, the parent distribution for experimental errors is presently unknown. It was therefore decided that a standardized procedure for the estimation and reporting of statistical errors should be developed as a short-term solution. The first step towards achieving this goal was a survey of presently used methods for error analysis. The survey was conducted in the second half of 1997, and the results are summarized on-line at:

<http://ixs.iit.edu/survey/errors/index.html>

It should be noted that this is an open project, and all authors of EXAFS software packages who wish to be included should provide the relevant information requested in

the on-line document. Contact persons for submitting information are provided at the above URL. From the survey it became apparent that virtually all existing packages use very similar methods based on the same ideas, but no two packages use the same set of definitions, particularly with respect to normalization of the χ^2 function and estimation of confidence limits. This has the unfortunate effect of making it impossible to directly compare error estimates obtained with different software. The Error Group therefore developed guidelines that may be used by authors of software packages to gradually standardize error reporting methods. The proposed guidelines are based on the currently accepted practices, and can ultimately be generalized to include the effects of experimental and other errors when such information becomes available. The guidelines, will be finalized at the IXS S&C committee meeting at XAFS XI in Japan, and will be made available for discussion, comments and possible modifications, followed by adoption as a policy of the IXS by the Executive Committee.

3.2. Statistical Tests (F-Tests)

While refining EXAFS models by non-linear least-squares refinement, it is often useful to improve fits by searching other minima, adding new parameters, or changing some atom types. The appropriateness of a fit improvement should be evaluated quantitatively using a statistical test. The use of statistical F-tests for EXAFS data analysis was initially described by Joyner et al., J. Phys. **C20**, 4005 (1987) and also by Filipponi, J. Phys. Cond. Matter **7**, 9343 (1995). Some members of the Error Group, and of the ICSC in general, felt that the F-test was of limited utility, and any future work on it should clearly demonstrate the limits of applicability, as well as outline clear procedures for using the test. Work on this project has begun and published in the XAFS X proceedings [Michalowicz and Vlais, J. Syn. Rad., **6**, 1317, (1999)]. Even without the use of a quantitative statistical test, it is possible to propose simple rules of thumb:

a) A $(\Delta\chi)_{min}^2$ improvement should always take into account the number of fitted parameters.

b) The reduced $(\Delta\chi)_\nu^2 = (\Delta\chi)^2/\nu$ where ν is the number of degrees of freedom used in the fit is a sufficient quantitative criterion.

3.3. Sources of Error

A preliminary listing of various sources of error has been prepared. While this list is far from complete, it identifies the more common sources of error. The preliminary list given below does not attempt to prioritize the importance of the errors, but merely groups them into several broad categories. Prioritization is an action item for future work.

3.3.1. Sample Preparation and Characterization

- Is what is measured what you think was measured? Was the sample checked by other means before and after the measurement? Is the sample susceptible to radiation damage (particularly biological samples). If the material was crystalline,

was it checked with x-ray diffraction (there have been reports of chalcogenide crystals rendered x-ray amorphous by grinding in a dry mill)? If the sample is pH dependent, at what temperature was this pH dependency measured? For SEXAFS, were LEED and Auger measurements done?

- Sample homogeneity. Was the sample made several times and measured? How reproducible is the amplitude information in the EXAFS signal?
- Sample thickness and particle sizes. These are discussed in a number of places. For example, see Stern et al., Phys. Rev. B, **23**, 3781 (1981), and Lu et al., Nucl. Instrum. Meth. **212**, 475 (1983).
- Texture effects in powders and/or preferred orientation in polycrystalline samples (non- cubic symmetries only).

3.3.2. Beamline Hardware and Software

- Phase contrast structure in the X-ray beam due to windows in the beam path. This structure is energy dependent and for small slits can result in I_0 structure which does not cancel.
- Temperature changes in ion chambers of a few degrees over an EXAFS scan (e.g., if LN₂ boiloff is turning on and off).
- Differences in ground levels inside and outside hutch (depends on cabling). Crosstalk between motors cables and signal cables.
- Errors in the energy scale, both calibration errors and resolution.
- Serial correlations (measurement results for neighboring data points that are not independent) induced by the use of Fourier transforms and/or data interpolation.
- Horizontal shifts in centroid of beam during fluorescence measurements (I_0 not sensitive, I_f sees variations in solid angle that can be comparable to XAFS). This could be a problem with undulators (depending on where the monochromator is on the undulator peak), or with a fixed exit monochromator for which second crystal translation introduces a yaw wobble.

3.3.3. Experimental Setup

- Harmonics, noise, glitches, quantization (counting statistics), non-linearity of the detectors, monochromator systematics, sample alignment. These are discussed in:
<http://gbxafs.iit.edu/training/Noise.pdf>
- Condensation and icing on windows.

- Varying requirements of fluorescence, electron yield, reflectivity, and other “special methods.” A discussion of many aspects of systemic error analysis and avoidance in fluorescence EXAFS are available at

http://gbxafs.iit.edu/training/errors_in_fluorescence.pdf

- Dilute samples: stray fluorescence from sample chamber, cells, filters, slits. Forward scatter from beam defining slits hits sample cell.
- Solid-state detectors: detection of stray fluorescence from reference foils placed after the *I* chamber; dead-time corrections, whenever applicable.
- Aliasing of high frequency components in raw data (real or spurious), due to undersampling of the data.
- The effects of drift on averaging techniques.

3.3.4. Data Processing

- Pre and post-edge modeling (including multi-electron excitations); normalization to unit step height; deglitching.
- Energy-dependent corrections: McMaster-type corrections, corrections for sample self absorption, fill gas sensitivity, detector dead time.
- The possible inaccuracy of the McMaster corrections over the first few hundred eV after the absorption edge. In particular, comparison to other tabulated coefficients currently believed to be more reliable, e.g., the Cromer-Lieberman values, should be performed.
- No precompensation for very different Debye-Waller factors in standard and unknown. (Standard could be empirical or theoretical, but should be transformed exactly same *k*-range, same width in *r*-range as unknown).

3.3.5. Analytical Procedures

- Data comparison with experimental model compounds: how good is the standard (errors in crystal structure determination); how related is the standard to the unknown; are anharmonic/asymmetric corrections necessary; how relevant is multiple scattering?
- Data comparison with theory: systematics and limitations in the one electron picture; systematics due to approximations employed, e.g., muffin-tin approximation, exchange- correlation potential; accuracy of the determination of an “empirical” S_0^2 , and its transferability and dependence on the specific conditions used to determine it (*k*-ranges, *k*-weight, error estimates, etc.); energy dependence of S_0^2 .
- Neglecting anharmonicity; neglecting to vary *R* in the $1/R^2$ term; the small but systematic correction $-\sigma^2/R$, especially in case with large disorder.

- Serious relative errors due to parameter correlations, especially in cumulant and/or multi-shell fits.

3.4. Determination and Modeling of the Error Distribution

A consensus was reached that it is necessary to perform a round robin of as many EXAFS beamlines as possible with a standardized set of samples under “optimal” experimental conditions in order to estimate the parent distribution of experimental error. Such information will subsequently be used in Monte Carlo simulations to determine significance levels to be used in the estimation of errors in the fit parameters.