

WinXAS: a Program for X-ray Absorption Spectroscopy Data Analysis under MS-Windows

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WinXAS is a new X-ray absorption spectroscopy (XAS) data-analysis program. It runs under the operating system MS-Windows 95/NT and offers several unique features. It has a user-friendly graphical environment and is capable of reading a variety of data formats. It contains a number of useful numerical algorithms beyond those used in conventional XAS analysis and offers a simple interface to the *ab-initio* theoretical code *FEFF*. The availability of fast *macros* in *WinXAS* makes it particularly useful for on-line data examination at synchrotron radiation facilities during XAS experiments as well as for the analysis of multiple-scan data such as those from time-resolved experiments.

Keywords: XAFS data analysis; FEFF; time-resolved studies; energy-dispersive XAS.

1. Introduction

Regardless of the system under investigation, basically every XAS (X-ray absorption spectroscopy) data analysis begins with the visualization of experimental spectra and basic reduction steps such as energy calibration, glitch removal and background subtraction. Whereas instrumentation and theoretical developments have been considerably improved in the past few years, the availability of versatile graphical data-analysis programs that exceed the requirements of conventional XAS analysis does not seem to have caught up with this evolution. Furthermore, with standard XAS beamlines equipped with fast scanning options (Quick-EXAFS) or energy-dispersive XAS beamlines providing time resolution in the sub-second range, XAS is used in a growing number of time-resolved experiments and kinetic studies. Since the number of spectra measured during one multiple-scan experiment can amount to several hundred, such investigations demand data-reduction software prepared to cope with large data sets. This paper presents *WinXAS*, an XAFS data-analysis program for MS-Windows that combines a versatile and efficient graphical user interface with numerous XAS analysis capabilities, useful numerical subroutines, and automated analysis features for multiple-scan data. In the following, the numerical procedures and graphical routines that comprise the basic modules of *WinXAS* are described.

2. System requirements

WinXAS runs under the 32-bit operating system Microsoft Windows 95/NT on IBM-compatible personal computers

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(PC). A Pentium 100 MHz processor (or comparable), 16 Mbytes RAM and SVGA monitor resolution are recommended as a minimal configuration for fast data analysis. Owing to general MS-Windows features, the appearance of most Windows programs is similar with respect to their basic functions, and getting started with *WinXAS* should be simple even for novice users. A PC mouse is used to select single menu entries, to input values directly from several dialog boxes, and to change XAFS function parameters interactively.

Information about the latest *WinXAS* version as well as how to register can be obtained from the World Wide Web (http://ourworld.compuserve.com/homepages/t_ressler). The program is distributed together with on-line help, a manual in postscript format, and a graphical visualization program for molecules and clusters (*RasMol*; Sayle, 1995).

3. Basic I/O and graphical features

WinXAS is capable of reading various ASCII file formats from a number of XAFS beamlines. Multiple-column ASCII files are automatically recognized and the user can choose the proper column number for photon energy, I_0 , I_1 and I_2 to calculate the absorption spectrum and reference spectrum (with I_0 , I_1 and I_2 being the beam intensity measured before and after the sample, and after the reference, respectively). Therefore, a separate conversion program for data from various beamlines may turn out to be unnecessary in most cases. *WinXAS* stores data by default in a binary format to save storage space and access time. As a user option, spectra can also be saved in a two-

column ASCII format for data transfer. Both formats are kept simple and are well documented.

One of the outstanding features of *WinXAS* is its user-friendly graphical interface. *WinXAS* offers a full visualization of results and intermediate steps during data reduction. A maximum of four spectra can be processed simultaneously, each in a separate graphic window, and plots from each window can be superimposed and compared at any time. Moreover, each of the four graphic windows contains four internal data arrays that are used to hold and display intermediate analysis steps and final results. Thus, every data-reduction step can be undone, and input and output of each analysis procedure are available for comparison. Furthermore, *WinXAS* plots can readily be copied to common word processors.

4. Numerical subroutines

Numerical subroutines implemented in *WinXAS* include a selection of common and useful algorithms to calculate integrals, derivatives, roots, Fourier transformation, smoothing, and least-squares refinement of a variety of profile functions. All of these algorithms can be employed independently from an ongoing XAS analysis at every step of the reduction procedure. Each numerical subroutine is documented in the *WinXAS* manual and details such as constraints, limitations and accuracy can be obtained from the cited literature (Press *et al.*, 1989; Engeln-Müllges & Uhlig, 1996). Profile functions can be composed of a variety of built-in functions (*i.e.* Gaussian, Lorentzian, Voigt, trigonometrical, polynomials *etc.*). *WinXAS* also allows one to add or multiply profile functions and data as well as to apply profile functions to the abscissa or ordinate of a spectrum. In this way, difference files can be calculated and spectra can be normalized.

5. Conventional XAS data analysis

Since *WinXAS* does not consist of separate analysis modules, all numerical procedures and graphical features can be used at any stage of XAS data analysis. Therefore, *WinXAS* exceeds the step-by-step approach of earlier analysis programs. Data-reduction features such as smoothing, convolution, XANES profile fitting, linear combination XANES fitting using experimental spectra (mixture analysis) or difference file techniques (Vaarkamp *et al.*, 1993) extend the implemented conventional XAFS analysis capabilities. Moreover, different reduction procedures can be applied to the same spectrum in different windows and respective results can be compared. Fig. 1 displays the *WinXAS* user interface and four different examples for its XAS data-analysis capabilities.

WinXAS offers multiple subroutines for most of the conventional XAFS data-reduction procedures. However, certain recommendations for the analysis of XAFS spectra have been implemented (Teo, 1986; Koningsberger & Prins, 1988). All necessary steps for conventional XAS

data reduction can be carried out [background subtraction (Victoreen, one or two polynomial), E_0 determination (first and second derivative, XANES profile function fitting), atomic absorption μ_0 (cubic spline fitting, polynomial fit), fast Fourier transform (several window functions, variable step width in R space)]. Furthermore, experimental phase shifts and backscattering amplitudes obtained from reference compounds, as well as theoretical phases and amplitudes, can be used to perform single-scattering plane-wave XAFS refinements. Higher cumulants can be added to the standard XAFS formula to account for a non-Gaussian distribution in thermal disorder. XAFS refinements can be carried out in k space or in R space.

During all the above-mentioned analysis steps a proper visualization of results and their dependence on the various parameters is provided. The atomic absorption (μ_0 -fit) window, for instance, not only displays the spectrum and the refined cubic spline, but also the resulting XAFS function $\chi(k)$, the first derivative of the cubic spline, and the magnitude and imaginary part of the Fourier-transformed $\chi(k)$. Therefore, the user has maximal information at hand on how changing the number of nodes for the spline, the weighting scheme or the section of the spectrum affects the resulting $\chi(k)$ and $\text{FT}[\chi(k)]$. In the case of an XAFS simulation using experimental or theoretical phases and amplitudes, single-function parameters can be changed interactively. In a corresponding dialog box each XAFS parameter can be changed stepwise, while after each step the effect on the theoretical $\chi(k)$ is displayed immediately. This procedure is very much suited as a teaching tool to visualize the dependence of the overall shape of $\chi(k)$ or $\text{FT}[\chi(k)]$ on the various structural or scattering parameters.

Additionally, every data-reduction step in *WinXAS* can be recorded in a macro. A complete XAS data analysis, containing background correction, μ_0 fitting, Fourier transform and XAFS refinement, can basically be carried out in one step. After recording, these macros can be applied conveniently to a large number of spectra measured under similar conditions.

6. FEFF interface

WinXAS contains an interface to the *ab-initio* multiple-scattering XAFS code *FEFF* by Rehr *et al.* (1992) (*FEFF* is not part of the *WinXAS* package and has to be obtained separately). In the recent past, *FEFF* has proven to be a reliable and user-friendly theoretical XAFS code. However, regardless of the operating system used, *FEFF* provides no graphical visualization of input or output data for analysis of experimental spectra. Although numerical tools in addition to *FEFF* are available (Stern *et al.*, 1995), they basically also lack graphical visualization.

The *WinXAS FEFF* interface enables users to perform an XAFS analysis using *FEFF*-generated theoretical phases and amplitudes. *WinXAS* allows the user to choose all

necessary paths from the *FEFF* output file 'FILES.DAT' which contains the names of all single-output files that belong to the scattering paths included in the calculation. The selected *FEFF* phases and amplitudes can be employed in a multiple-shell XAFS simulation or refinements in both k space and R space.

Furthermore, *WinXAS* offers several schemes to correlate or constrain XAFS function parameters during the refinement (e.g. Debye–Waller factors of different paths can be refined the same or, in the case of a multiple-scattering path, can be forced to be equal to the sum of the single-scattering-path Debye–Waller factors; coordination numbers of two paths in an octahedral environment can be constrained to have a sum equal to six; and others). The output of an XAFS refinement includes structural and scattering parameters, standard deviations, correlation matrix, and the graphical fit residual. The Fourier trans-

form of the fit residual, the experimental spectrum and the theoretical $\chi(k)$ are also displayed.

In addition to XAFS refinements, *WinXAS* offers several features to facilitate *FEFF* calculations. Running *FEFF* on a PC involves setting up the proper input files in an editor, executing *FEFF* and afterwards changing to a graphic program to display the calculated XAFS function. With *WinXAS*, these steps can be carried out in a single program's environment. After *FEFF* input files have been set up in an editor, the program can be launched directly from *WinXAS* and, after the calculation is completed, the resulting $\chi(k)$ is loaded and displayed instantaneously for further analysis or comparison with experimental data.

Furthermore, *WinXAS* supports *RasMol*, a simple but effective molecular-structure viewing program (Sayle, 1995). *FEFF* input files are converted into three-column xyz files that can be read from *RasMol* and allows mole-

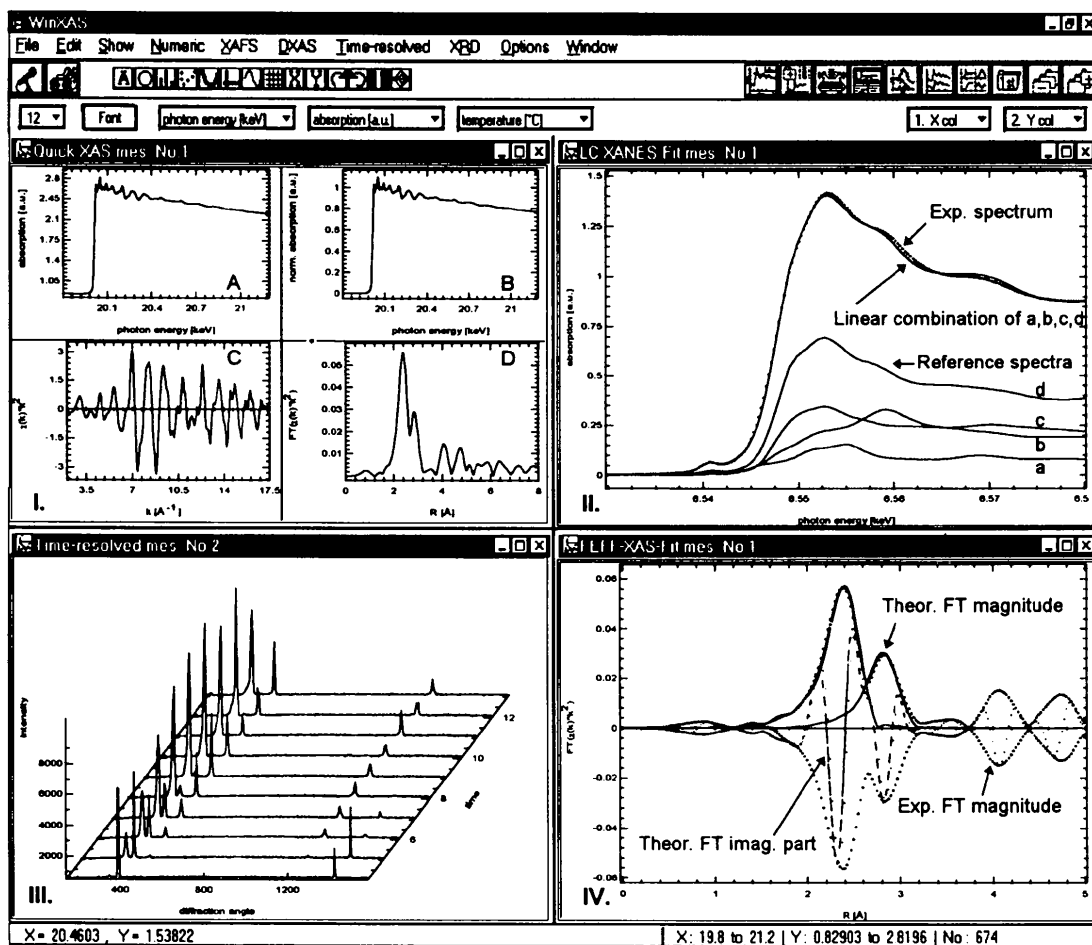


Figure 1

'Screen-shot' of the *WinXAS* program for XAS data analysis showing the user interface as well as four graphic windows containing examples for analysis capabilities. Window I: 'Quick-XAS' data analysis of an as-measured absorption spectrum (A). The 'Quick-XAS' option represents an automated data-reduction procedure. Experimental spectra can be analyzed on-line by pressing a single button on the *WinXAS* interface. The algorithm yields the normalized and background-corrected spectrum (B), the extracted XAS function $\chi(k)$ (C) and the Fourier transformed $\chi(k)$ (D). Window II: Least-squares XANES fit. The experimental XANES (dotted) can be simulated by a linear combination of four reference compounds [a (0.1), b (0.21), c (0.23) and d (0.46)]. Window III: three-dimensional plot of diffraction data from a time-resolved experiment. In a subsequent analysis, *WinXAS*'s macro capabilities can be used to determine peak shifts and intensity variations with time. Window IV: Two-shell XAS refinement in R space using *FEFF* theoretical phases and amplitudes. The plot shows the FT magnitude and imaginary part for the experimental (dotted) and theoretical (solid) curve as well as the magnitude for both single shells.

cules or clusters to be displayed in colours, rotated and printed. The combination of *WinXAS* and *RasMol* not only makes a convenient tool, it can also help novice users to understand the concept of nearest-neighbour shells, of different coordination geometry and distortions, and of linear multiple-scattering paths that will have a particularly strong contribution to the theoretical XAFS function.

7. Time-resolved experiments

The analysis of XAS data obtained from time-resolved experiments can become a very tedious task due to the large number of consecutive spectra. *WinXAS* offers several features to treat the large amount of data obtained from time-resolved experiments. Considering the number of spectra from a single run, data reduction of each spectrum by hand appears to be inefficient. Since many analysis steps have to be carried out similarly for each spectrum, efficient data treatment requires the possibility of applying a sequence of analysis steps in a serial procedure. *WinXAS* can record single data-reduction steps into a macro and execute this macro to analyze each individual spectrum out of a large data set. All numerical and XAFS algorithms contained in *WinXAS* can be used this way. Additionally, several spectra can be averaged to improve data quality. Moreover, a serial data treatment can be performed at an early stage of a time-resolved experiment investigation. Besides the fact that *WinXAS* aims at time-resolved XAS investigations, it can be employed in a variety of experiments that produce a large number of consecutive spectra or patterns that require serial treatment.

8. Energy-dispersive XAS

The analysis of XAS data measured in an energy-dispersive mode (Hagelstein *et al.*, 1989) requires some additional reduction steps compared with conventional XAS data analysis. In contrast to a standard double-crystal monochromator, where the energy range is scanned stepwise by changing the Bragg angle of both crystals, the dispersive spectrometer applies a bent monochromator crystal. The absorption signal is then recorded on a position-sensitive detector.

The major difference between conventional and energy-dispersive XAS data reduction lies in the energy calibration of the measured absorption spectra. In order to calibrate dispersive XAS spectra, a polynomial has to be calculated representing the energy-position correlation on the detector and converting the measured absorption spectra to photon energy. With *WinXAS*, the polynomial coefficients can be determined from an automated comparison of the measured metal foil with a calibrated metal-foil spectrum obtained at a standard XAS beamline. If DXAS data and the reference metal-foil spectrum are available in a comparable quality, this procedure usually

results in a reliable energy calibration of dispersive XAS data. More detailed descriptions on using *WinXAS* for energy-dispersive XAS analysis can be found elsewhere (Ressler, 1995, 1997). Although *WinXAS* was originally written for the DXAS beamline at HASYLAB, Hamburg, all functions are generalized enough to be used at any other DXAS stations. Experimental data can either be used as measured or be converted into a binary *WinXAS* format.

9. Summary

WinXAS is an XAS data-analysis program for computers running MS-Windows 95/NT. The most important feature of *WinXAS* is the versatile graphical user interface. *WinXAS* allows a maximum of four data files to be processed at a time and results can be superimposed and compared. Furthermore, *WinXAS* represents a good educational tool due to the immediate graphical response on changes in, for instance, XAFS fit parameters, k weighting, number of nodes for cubic-spline fits, and much more. Thus, *WinXAS* can help to gain insight into the interaction of atomic distances, disorder parameters, or number of shells, and their influence on the XAFS function $\chi(k)$ and hence the observed experimental signal.

WinXAS contains all necessary numerical algorithms and procedures for conventional XAS data analysis and offers an interface to the *ab-initio* theoretical code *FEFF*. Moreover, many additional techniques that exceed conventional data reduction can be carried out, such as difference file technique, experimental XANES linear combination fits (component analysis), XANES profile fitting, and using *FEFF* theoretical phases and amplitudes for XAFS refinement. Owing to an open and flexible data file structure, *WinXAS* can read a variety of multiple-column files from different XAS beamlines without previous conversion.

Besides numerical and conventional XAS features, *WinXAS* contains several routines for the analysis of energy-dispersive XAS data. Furthermore, *WinXAS* macros can be employed in a serial treatment of a large number of consecutive spectra such as those obtained from time-resolved experiments.

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