XANES dactyloscope

A program for quick and rigorous XANES analysis for Windows

Users Manual and Tutorial

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1 Introduction

1.1 What is XANES dactyloscope?

XANES dactyloscope (XD) is a program for data analysis of XANES spectra. It includes:

- energy calibration,

- deconvolution of absorption coefficient with monochromator resolution curve and/or core-hole lifetime broadening curve,

- transformation to a new equidistant grid,

- pre-edge background subtraction,

- correction by a user-defined function or fluorescence self-absorption correction for thick or thin samples,

- normalization,

- base line subtraction for analysis of pre-edge peaks,

- principal component analysis or target transformation,

- fitting by a user-defined formula (usually, a linear combination fitting) with advanced error analysis.

XD does not include ab-initio XANES calculation. Also, XD does not produce publication quality graphs. It only exports column files to be loaded by Matplotlib, QtiPlot, Origin etc.

Although several ab-initio XANES calculation codes have been successful in reproducing some particular spectra (mostly, of metal samples), the quantitative treatment of XANES still remains a challenging problem. For this reason XANES is mostly used for "finger-print" analysis which considers specific spectroscopic features ("finger-prints"): pre-edge peaks, white lines, edge shifts etc. for identifying the chemical states and/or local atomic symmetry. This explains the name of the program XANES dactyloscope.

1.2 What makes XANES dactyloscope special?

Any time, all curves and their changes under processing are visual. The visualization is not only a matter of convenience; it serves for the ultimate quality check of experimental data and processing steps by the program user.

XD is also useful for quick quality check during your beam time at synchrotrons. A simple drag-and-drop action reveals in a second the spectrum quality and reproducibility in E-space.

XD offers the most comprehensive Principal Component Analysis and self-absorption correction procedures as described below.

1.3 System requirements

XANES dactyloscope runs on all 32- and 64-bit Windows systems. It can run under Linux with Wine. The minimum screen resolution is recommended as 1024×768.

Originally, XANES dactyloscope was a 16-bit program that could not run on 64-bit Windows. I thank Roman Chernikov (Hasylab at DESY) for making the 32-bit build.

1.4 About this manual

This file describes the program XANES dactyloscope, build 5.30. It is essential to unpack the archive with examples. The examples *.xpj can be simply loaded by associating them with XD. I have tried to explain all the aspects of the program that may be useful to its user in setting up his or her analysis of XANES spectra.

2 Opening data files
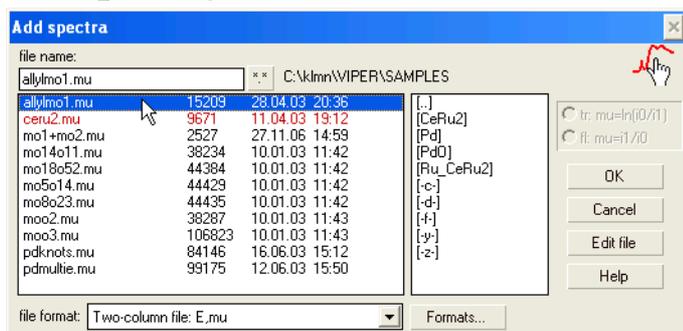
You can select multiple files using Ctrl or Shift buttons or by mouse dragging. The name of the last opened file is colored by red. The design of the Load data dialog is old fashioned; the files are always sorted by name whereas frequently time sorting is more convenient. Therefore I recommend drag-and-drop technique combined with your favorite file commander or Explorer. This way is very useful at a beam time when you quickly add a newly measured file to the already opened ones by simple drag-and-drop from your time-sorted directory. I use the Load data dialog mostly to set up new data formats and, sometimes, to manually select the file format. The latter is needed when the same file has transmission and fluorescence signals and one wants to load both. In this case one needs two formats described and, of course, only one of the two will be recognized automatically.

Important: you can load multiple files and do drag-and-drop only provided your file format is recognized automatically (i.e. when you see the format name updated correctly in the 'Add spectra' dialog after you have clicked a file name).

The number of the loaded spectra is restricted by your RAM.

2.1 File formats

Look first at your data file in a common text editor.
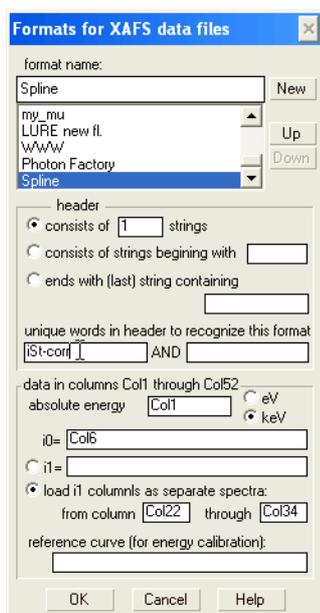
Specify the file header. Give one or two sub-strings contained in the header for automatic recognition. If your file is recognized incorrectly, try to find other unique sub-strings or use button 'Up' to place your format earlier in the recognition queue.

In the description of the data columns one can use (almost) any function of variables Col1 … Col52. For instance, one can load several fluorescence signals i1 as, say, Col5+Col6+... or, better, one can load these signals as separate spectra for better visual quality checking.

The internal energy unit is eV. Therefore if your energy unit is different, you should do a transform, like Col4*1e+6. For keV unit there is a dedicated option.

The 'reference curve' is only needed for energy calibration and can be left empty. Usually, this is the absorption coefficient of a reference foil placed between the 2nd (i1) and the 3rd (i2) ionization chambers. Correspondingly, it is given by ln(Col$N$/Col$M$), where Col$N$ and Col$M$ represent i1 and i2 signals.

The format descriptions are saved in a text file formats.ini. If you want to transfer it to another computer, just copy it to the directory of the program executable file. You can manually merge various formats.ini files using common text editors; re-number then the strings properly.

2.2 Project files

The list of all loaded spectra together with the selected analysis steps can be saved in a project file. Project files can be loaded using 'Project/Load project' menu or by associating XD with the project files (*.xpj files).

Several example projects together with the associated data are provided in a separate archive.

3 Program interface
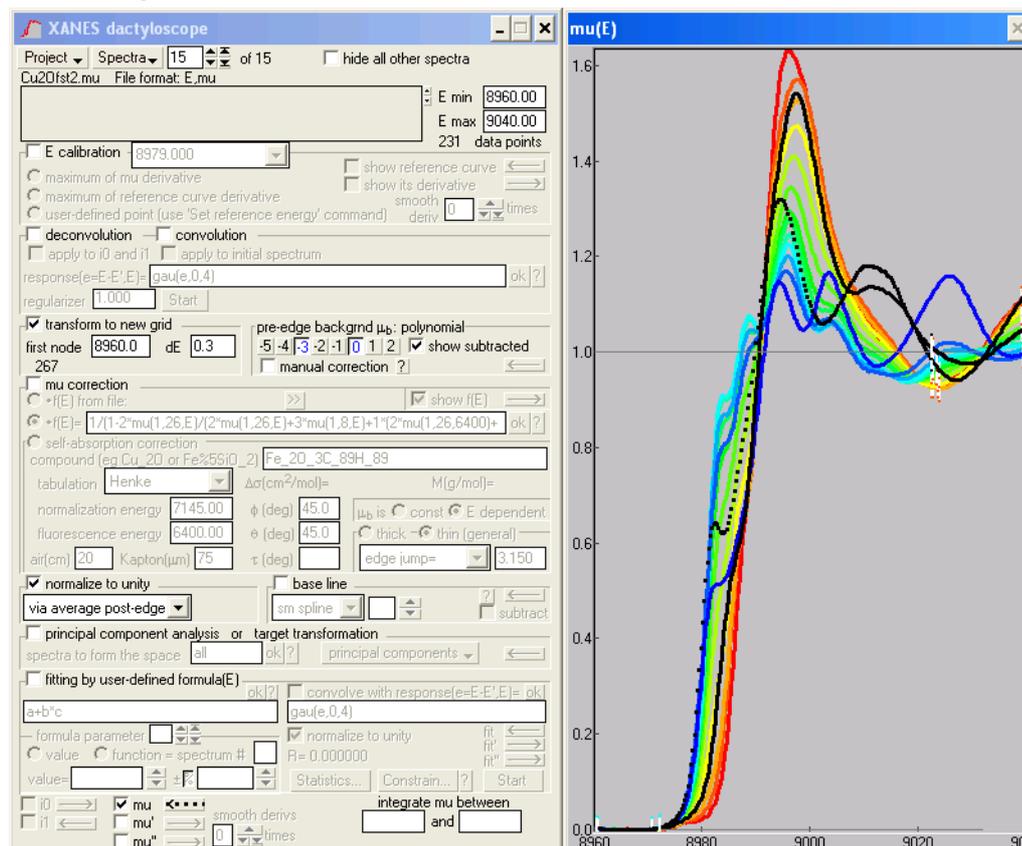
The program interface consists of the main dialog and the graph window. Use the pop-up menu in the graph window to use the most frequent commands, e.g. to restore the default zooming.

Use the 'Spectra' menu to switch between the loaded spectra, change their sequence, add or remove spectra, access the line properties etc.

Note that all the properties in the main dialog refer to the *current* spectrum. The current spectrum is also drawn in front of the others. When the graph is redrawn, the current spectrum blinks. In this way you can easily identify the current spectrum when you click in the graph window to redraw it.

The arrow buttons ⟵ give access to the corresponding line settings and show to which Y axis (left or right) the particular line belongs.
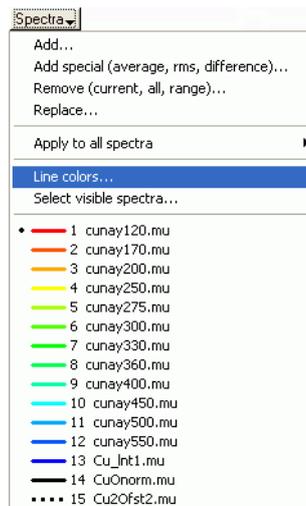
3.1 Line settings
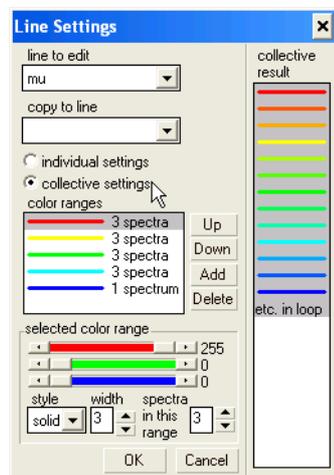
The line properties can be set collectively by specifying the color ranges. Within each range, the specified number of spectra are evenly spaced in the RGB color space towards the next color range. If the range is single, all the lines of a given kind will be equally colored for each spectrum.

Every line of every spectrum can have individual settings. You can decide whether to switch from individual to collective settings (or back) only for the current spectrum or for all spectra. This depends on whether you access the line settings from the individual arrow buttons (⟵) or from the Spectra menu.

The 'dots' line style puts dots not equidistantly but at the data points.
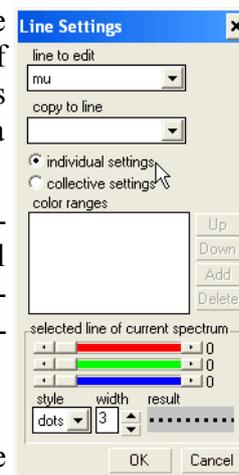
3.2 Selecting visible spectra

The spectra can be selected for viewing in the list of spectra. Use Ctrl/Shift buttons for multiple selection.

Another way of hiding spectra for clearer view is by using the check button 'hide all other spectra' at the top of the main dialog. This option displays only the current spectrum and overrides the selection (if any) in 'Select visible spectra' dialog.

4 Energy calibration

If the absorption spectra are measured in transmission, it is a common practice also to simultaneously measure the foil. Then the energy axis can be checked for reproducibility and corrected if needed.
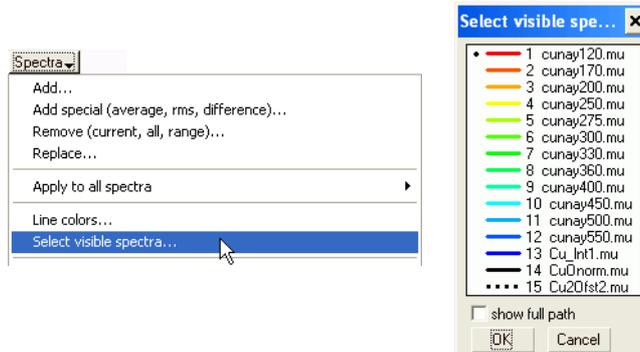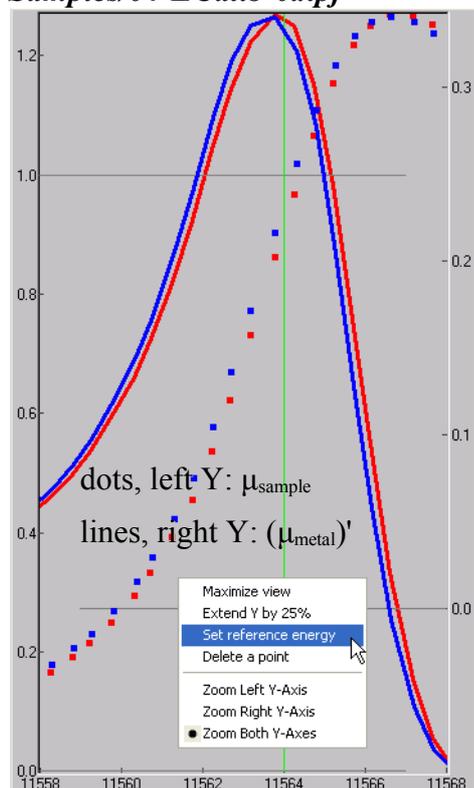
If your file format describes the reference curve, you can visualize it or its derivative in this section of the main dialog. Zoom in the derivative peak, as seen on the screenshots below.

to see this, open the project
Samples/04-ECalib-0.xpj

dots, left Y: μ_{sample}

lines, right Y: $(\mu_{metal})'$

Now select the reference energy. If your energy mesh around the absorption edge is finely spaced, just use 'maximum of reference curve derivative'. In the example shown the mesh was rough, 0.5 eV. Therefore such a calibration will not improve the energy reproducibility between the two spectra (try it!). In this case, much better calibration is given by manual positioning of the reference energy. For this, use 'user-defined point' and the pop-up menu command 'Set reference energy' (and put it somewhere close to the peak maximum) until you merge the reference curves of all spectra.

to see this, open the project
Samples/04-ECalib-1.xpj

dots, left Y: μ_{sample}

lines, right Y: $(\mu_{metal})'$
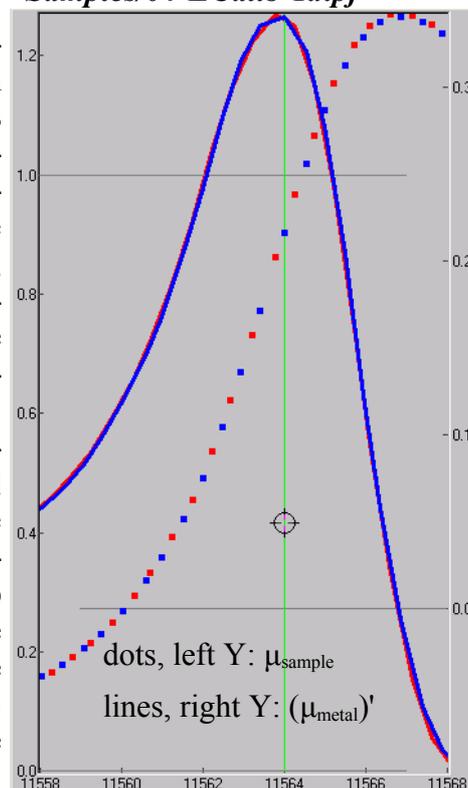
Tip: derivative of μ is used when the sample is a foil. In this case you usually do not put the foil also at the reference position. Then you use the derivative of μ for the sake of energy calibration but not the derivative of the reference spectrum.

The correcting energy shift is implemented as constant along the spectrum. In contrast to EXAFS, XANES spectra are short in energy. Therefore the constant energy shift is justified. In EXAFS analysis, *constant angle* and *constant lattice* shifts are more correct, as implemented in the program VIPER and explained in its manual.

5 Deconvolution of life-time and experimental broadening

See [Klementev 2001] for the description of the Bayesian deconvolution. This procedure is implemented in VIPER and XANES dactyloscope.
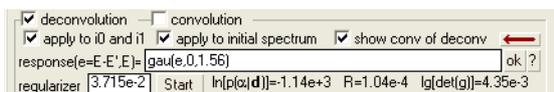
One can do several deconvolutions one after another (the check box 'apply to initial spectrum' must be off for this). This makes sense when one first does 'instrumental' and then 'lifetime' deconvolution. The former is typically of Gaussian kernel and is applied to the measured signals i_0 and i_1 separately. The latter is typically of Lorentzian kernel and is applied to $\mu(E)$.

There is a way for how to check the solution: after the deconvolution has been found, the back convolution is performed by true integration and the resulting deconvolved-convolved μ (I do not know if it is better to say "deconvoluted-convoluted") is displayed in the graph.
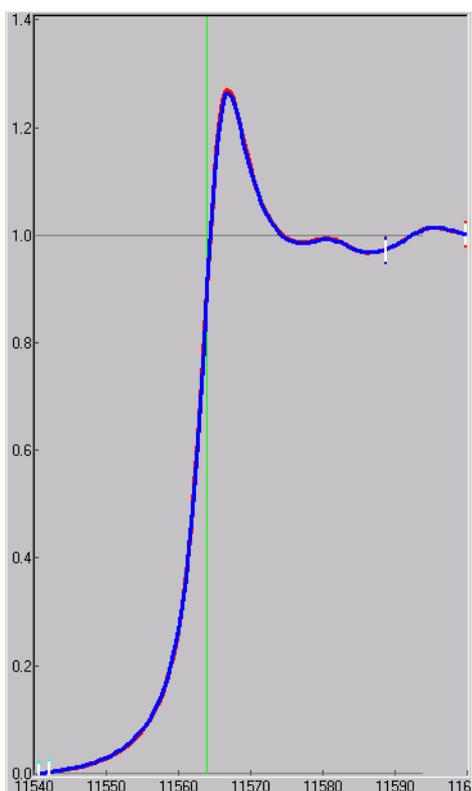
to see this, use the previously loaded example project *Samples/04-ECalib-1.xpj*

Here on the left there are two repetitions (red and blue) of the same spectrum. On the right the blue one is deconvolved with the parameters shown above (instrumental broadening with ΔE=3.7eV FWHM). The brown curve is the solution check, i.e. deconvolved-convolved μ. It coincides with the red one, which justifies the deconvolution.

You can see this also if you unselect the deconvolution made: the initial μ and the solution check must superimpose.
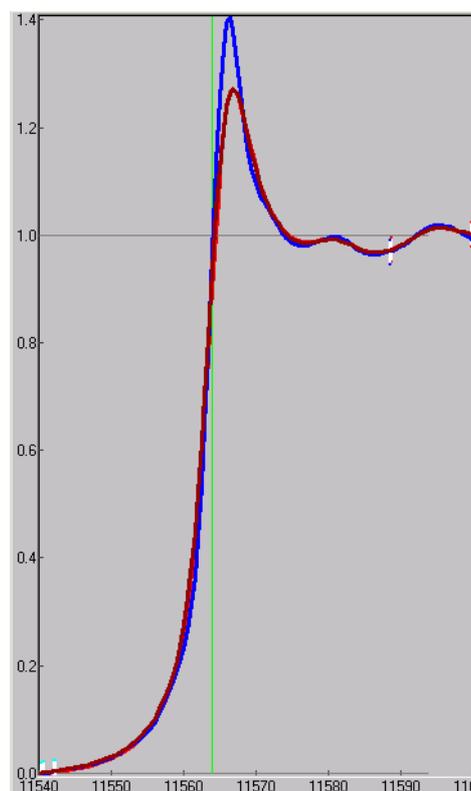
The Bayesian deconvolution depends on a parameter (regularizer), denoted as α. When it is small, the solution has rich fine structure, when it is big, the solution is smooth. You can change α and see that very different deconvolution solutions give successful solution checks. **There is no unique solution!**

5.1 How to select the regularizer?

One may try to define an optimal, in some sense, α. In [Klementev 2001] I proposed three possible ways for this. Unfortunately, what I did wrong, I did not consider the spectrum length scaling. For a full-length spectrum the optimal α must be the same as for its shorter piece. The third method does not fulfill this. It seems that the second method (the conservation of S/N ratio) is reasonable. The figures of merit introduced in [Klementev 2001] are reported in XD at the bottom of the deconvolution section of the main dialog. One can utilize them for (non-automatized) search for an optimum α.

6 Transformation to new grid

In several cases you need to transform your spectra to a common energy grid. For instance, you need this for Principal component analysis (PCA) or for averaging.

7 Subtraction of pre-edge background
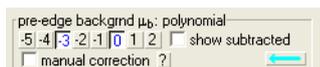
The pre-edge background is constructed by polynomial interpolation over the region specified by mouse (see the picture on the right). The polynomial law is given by the power buttons. For instance, the screenshot above shows the modified Victoreen polynomial $aE^{-3}+b$, where the coefficients are found by the standard least-squares method. The polynomial is then extrapolated over the absorption edge.

For absorption spectra measured in transmission mode, usually a Victoreen polynomial $aE^{-3}+bE^{-4}$ or a modified Victoreen polynomial is implied.

For absorption spectra measured in fluorescence mode, background subtraction is frequently not needed (unselect all the power buttons). More frequently a constant shift is sufficient (select button "0"). Sometimes the spectra exhibit a net growth with energy, which can be approximated by a linear law (select buttons "0" and "1"). Sometimes a severe background correction is needed, as explained below.
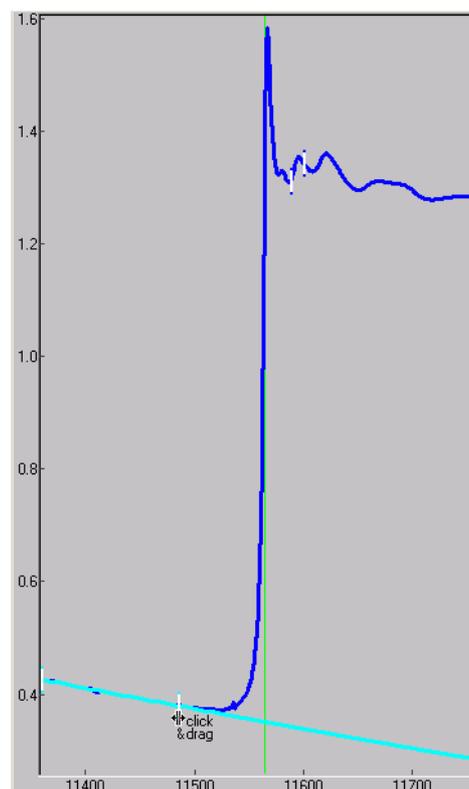
7.1 Corrections of pre-edge background

Some spectra behave strangely: they bend up or down, which makes the background subtraction difficult. One can correct such a behavior by introducing more powers into the background and/or by adding an extra point at a high energy.
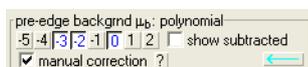
Checking the 'manual correction' option will put an extra point (you position it by mouse) which is additionally considered by XD in the least-squares method for finding the polynomial coefficients.
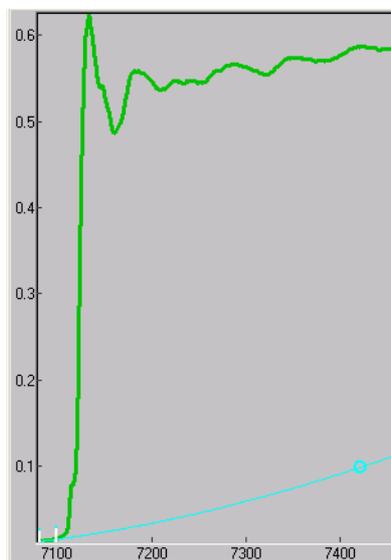
Consider a fluorescence experiment on a sample inside an in-situ cell. As you scan the x-ray energy up, the air paths and the windows become more transparent, thus the flux at the sample and the fluorescence flux grow high. This becomes even more pronounced when you normalize by the signal of the 1st ionization chamber: its signal goes down at high energy because its gas also becomes more transparent. Finally, the spectrum may look like on the left picture. For correcting this, select at least 3 polynomial powers and put an extra high energy point. The result after subtraction is shown at the right.
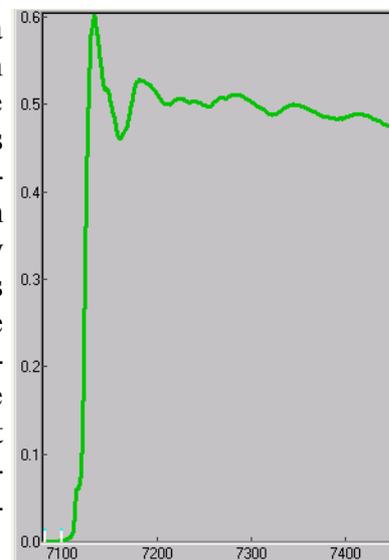
8 Self-absorption correction

Many papers have addressed the self-absorption effect. Most of them provided restricted correction. The early papers by [Goulon et al. 1982; Tan et al. 1989; Tröger et al. 1992] were limited only to the EXAFS case. The correction functions there had discontinuity at the edge and thus were not applicable to XANES. Moreover, those works provided corrections only for infinitely thick samples with an exception of [Tan et al. 1989] where also thin samples were considered but only as pure materials (e.g. single element foils).

The first self-absorption correction for the whole absorption spectra (also including XANES) was proposed with two different strategies by Eisebitt et al. [1993] and Iida and Noma [1993]. Eisebitt et al. [1993] estimated the two unknowns μ_{tot} and μ_X (see the notations below) from two independent fluorescence measurements with different positioning of the sample relative to the primary and fluorescence beams. An obvious disadvantage of this method is that it is solely applicable to polarization-independent structures (amorphous or of cubic symmetry). On the other hand, it does not require any theoretical tabulation, which is the case in the method of Iida and Noma [1993], who proposed the background part $\mu_{back} = \mu_{tot} - \mu_X$, to be taken as tabulated. The advantage of their approach is its applicability to any sample with only one measurement. Moreover, this method is applicable to samples of general thickness, not only to thick samples as required by the method of Eisebitt et al. [1993]. It is the method of Iida and Noma [1993] which is implemented, with some variations, in XD. The method was re-invented (i.e. published without citing Iida and Noma [1993]) by Pompa et al. [1995], Haskel [1999] and Carboni et al. [2005]. These three works, however, were simplified down to infinitely thick limit.

The correction was extended somewhat by considering a variable escape angle in order to account for the finite (not infinitely small) detector area: only in the synchrotron orbit plane, in EXAFS [Brewe et al. 1994] and also out of plane: in EXAFS [Pfalzer et al. 1999] and XANES [Carboni et al. 2005]. All three works operated in the thick limit. To my believe, detector pixels are always small in the sense that the self-absorption effect can be considered as uniform over each single pixel and therefore the correction can be done only for one direction towards the pixel center.

An interesting approach to correcting the self-absorption effect was proposed by Booth and Bridges [2005] who considered another small parameter, not the usual $\exp(-\mu d)$, which allowed simplifying the formulas also beyond the thick limit but the treatment was limited to EXAFS.

Another re-invention of the Iida and Noma method with calling it "new" was presented by Ablett et al. [2005]. The merit of that work was implementing the method without restriction to the thick limit and providing many application examples and literature references.

8.1 Description of self-absorption correction

The derivation of the fluorescence intensity can be found, with different notations, in almost all the papers cited above. Here it is repeated because XD adds some extra factors. The standard expression for the fluorescence intensity originated form the layer dz at the depth z is given by the trivial sequence of propagation and absorption (with neglected scattering):
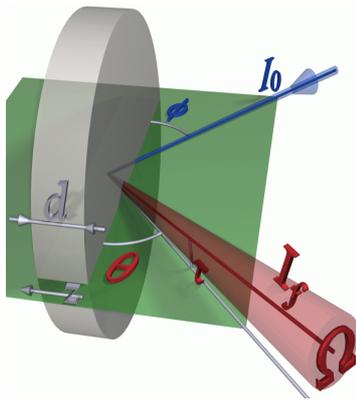
$$dI_f(z,E) = \underbrace{I_0}_{\substack{\text{primary}\\\text{flux}}} \underbrace{e^{-\mu_T(E)z/\sin\phi}}_{\substack{\text{primary x-ray}\\\text{transmitted to}\\\text{depth } z}} \underbrace{\mu_X(E)\frac{dz}{\sin\phi}}_{\substack{\text{absorbed in layer } dz\\\text{due to edge of interest}}} \underbrace{\epsilon_f}_{\substack{\text{transformed}\\\text{into}\\\text{fluorescence}}} \underbrace{\frac{\Omega}{4\pi}}_{\substack{\text{directed into}\\\text{solid angle } \Omega}} \underbrace{e^{-\mu_T(E_f)z/(\sin\theta\cos\tau)}}_{\substack{\text{fluorescence x-ray}\\\text{transmitted to detector}\\\text{from depth } z}}$$

where μ_T is the total linear absorption coefficient at the primary x-ray energy E or the fluorescence energy E_f, μ_X is the contribution from the edge of interest, ϵ_f is the fluorescence quantum yield – the probability to create a fluorescence photon from an absorbed photon. After integration over z from 0 to d:

$$I_f(E) = C\frac{\mu_X(E)}{\mu_T(E) + \mu_T(E_f)\dfrac{\sin\phi}{\sin\theta\cos\tau}}\left(1 - e^{-\mu_T(E)d/\sin\phi}e^{-\mu_T(E_f)d/(\sin\theta\cos\tau)}\right), \quad (*)$$

where the constant C includes all the energy independent factors and is treated as unknown because the actual solid angle is usually unknown and also because it implicitly includes the detector efficiency.

The total absorption coefficient is decomposed as $\mu_T = \mu_X + \mu_b$, where the background absorption coefficient μ_b is due to all other atoms and other edges of the element of interest. The constant C is found by equalizing all μ's at a selected energy E_{norm} ("normalization energy") to the tabulated ones. Now the equation (*) can be solved for μ_X at every energy point E, which is the final goal of the self-absorption correction.

When the sample is thick ($d \to \infty$), the exponent factors vanish. This "thick limit" approximation allows finding the μ_X by simple inversion of (*), without solving the non-linear equation, and is optional in XD.

8.2 Realization in XANES dactyloscope

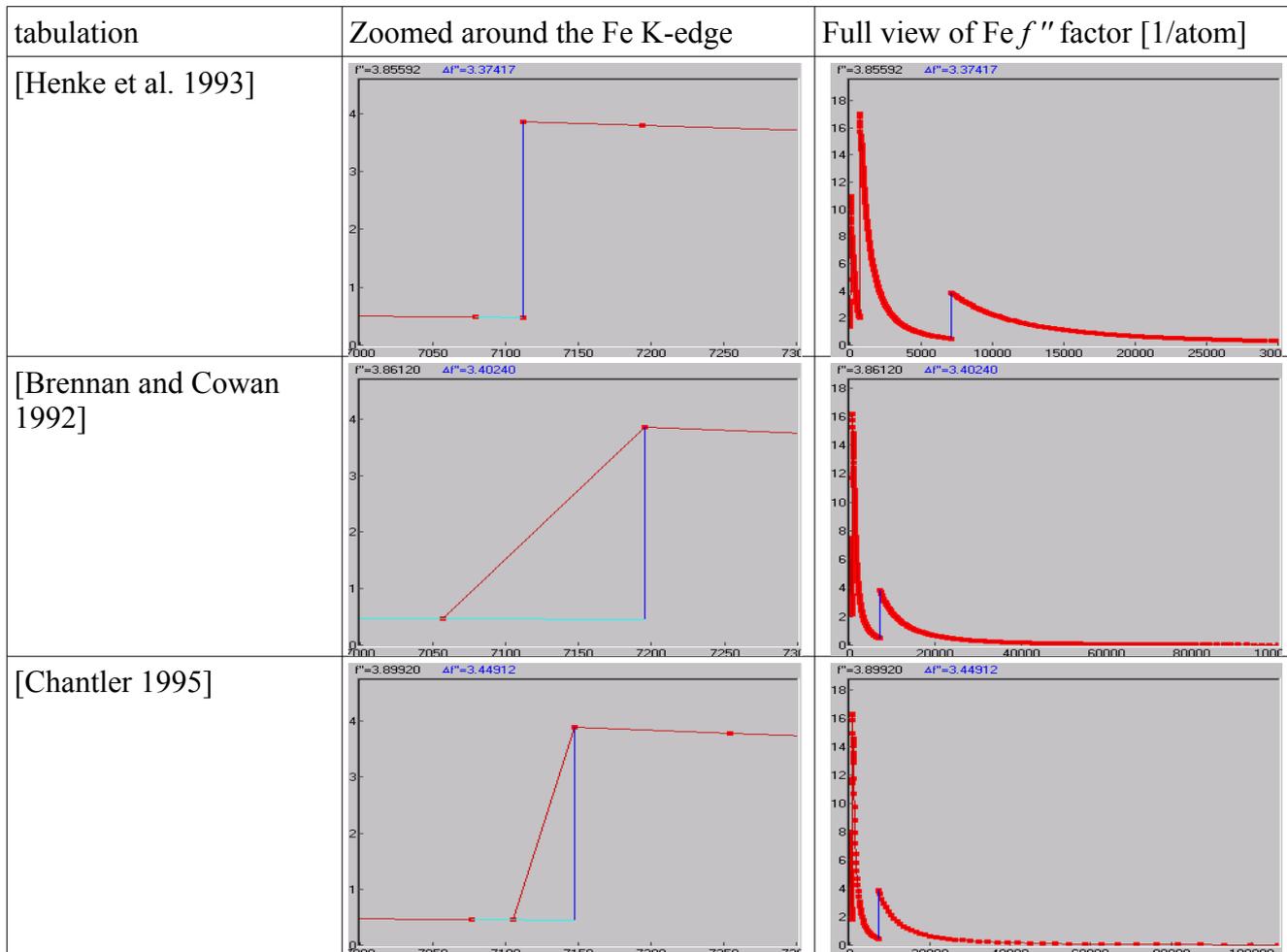### 8.2.1 Extended correction options

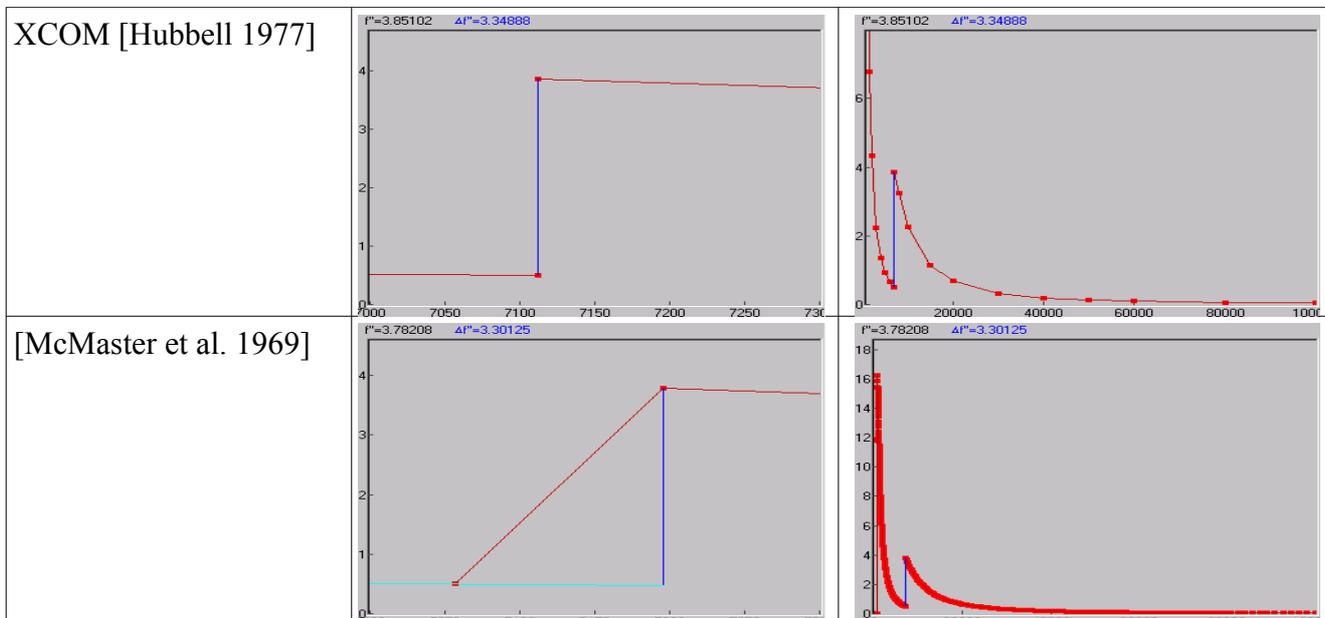Some of the options offered by XD are non-standard (extended):

1) The additional term $\cos\tau$ in (*) is not quite standard; one can also find it in [Carboni et al. 2005] and [Ablett et al. 2005].

2) Absorption by air and by Kapton foils in front of the sample can be taken into account (see the examples below). For this, the primary flux is multiplied by $e^{-\mu_{air}(E)d_{air}}e^{-\mu_{Kapton}(E)d_{Kapton}}$. The similar term at E_f is included into the constant C.

3) μ_b is usually taken to be energy independent. In XD it is energy dependent.

4) One can select among five different tabulations of absorption coefficients (actually, scattering factors f'') in XD.

8.2.2 How the tables of scattering factors are used?

In order to use the equation (*), it is prerequisite to know the sample stoichiometry, i.e. the molar weighting factors x_i for each atom type i in the sample. Then the linear absorption coefficient is proportional to the atomic absorption cross section σ_a: $\mu_X \propto x_X \sigma_{aX}$ and $\mu_T \propto \sum_i x_i \sigma_{ai}$. The atomic cross sections, in turn, are calculated from the tabulated scattering factors f'': $\sigma_a = 2 r_0 ch N_A f'' / E$.

Since all the tabulations do not contain the partial contributions of each absorption edge of an element but only the combined result of all atomic shells, an isolation of μ_X and the pre-edge background is required. In XD this is done by extrapolating the pre-edge region by the Victoreen polynomial. The polynomial coefficients are found over only two pre-edge points, as the tabulations are usually sparse. As illustrated below for each tabulation used, the edge jump is the difference between the first post-edge value and the extrapolated background:

tabulation	Zoomed around the Fe K-edge	Full view of Fe f'' factor [1/atom]
[Henke et al. 1993]	f''=3.85592 Δf''=3.37417	f''=3.85592 Δf''=3.37417
[Brennan and Cowan 1992]	f''=3.86120 Δf''=3.40240	f''=3.86120 Δf''=3.40240
[Chantler 1995]	f''=3.89920 Δf''=3.44912	f''=3.89920 Δf''=3.44912

|		
XCOM [Hubbell 1977]		
[McMaster et al. 1969]		

XD searches for an absorption edge (where the derivative is positive) within –250 eV from the specified normalization energy. When an edge is found, the jump in molar cross section is displayed in XD.

8.3   Examples

Load the example project **Samples/08-fe2o3_tr_fl.xpj**. It has 4 spectra of Fe_2O_3 (hematite) measured in transmission and fluorescence, each repeated twice to assure reproducibility. The sample is a 13-mm-diameter pressed pellet containing 11 mg of hematite mixed with 80 mg of polyethylene (PE) powder. The pellet was wrapped by adhesive Kapton foil.
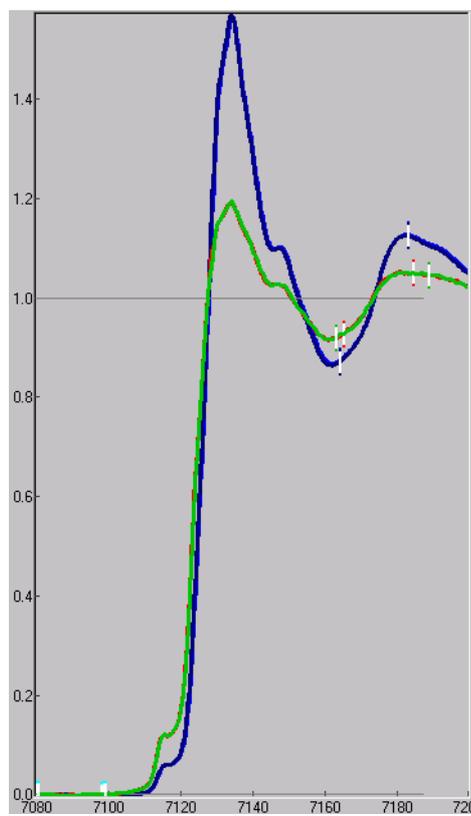

As seen on the left picture, the fluorescence spectra (red and green, overlapped) essentially differ from the transmission ones (light and dark blue, overlapped). As seen at the right, one of the two fluorescence spectra (green) is successfully corrected. Notice the EXAFS amplitude and the pre-edge peak.

The parameters for the self-absorption correction are seen in the screenshot below. It is essential to remember about the sample matrix or the supporting agent (here: PE) and to put its chemical formula as well. Here, the weight '83' of PE (CH_2) was calculated as
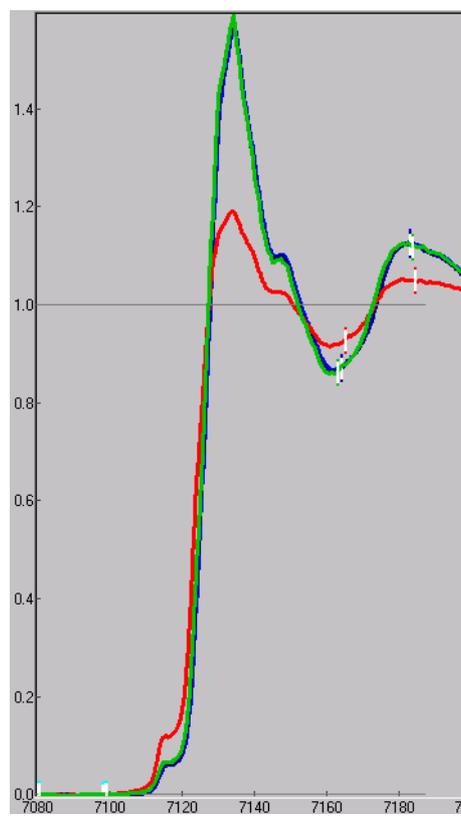
$m_{PE}M_{Fe2O3} / m_{Fe2O3}M_{PE} = 80mg160g/mol / 11mg14g/mol = 83$.
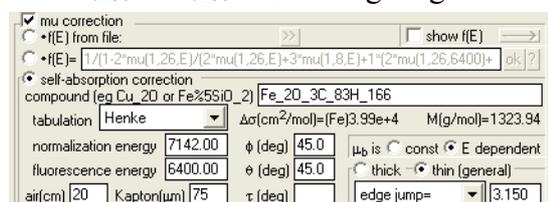
In order to use equation (*) for thin samples, one must provide the sample thickness. This could be the *physical* thickness; then one would need to know the sample density for calculating the linear absorption coefficient in the exponent. A more direct way is to use the *optical* thickness $\mu_T d$, or just
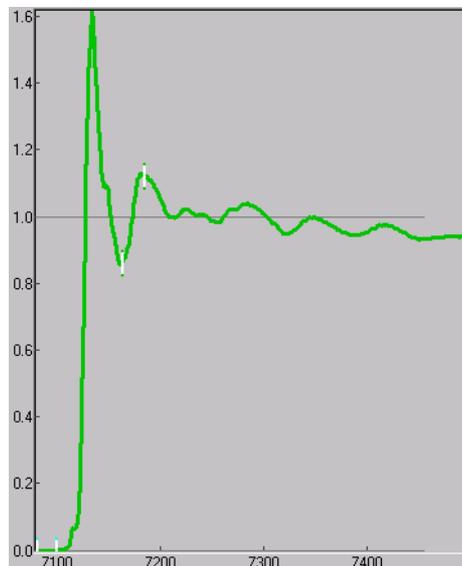
its jump at the edge, which is usually possible directly to measure in transmission spectra (remember, we are speaking here about thin samples, otherwise use the 'thick' option). If the physical thickness is known, which is usual for foils, use the program XAFSmass to calculate $\mu_T d$ or $\Delta\mu_X d$ from the sample composition, the thickness and density.

In the example above, the edge jump was found from the transmission spectra times $\sqrt{2}$ because the transmission spectra were measured at normal incidence whereas the fluorescence spectra were taken with the same sample at 45º. [For future versions of the manual: redo this example with simultaneously measured transmission and fluorescence]

Equation (*) is also useful for correcting the high-energy behavior of μ. This correction is especially relevant to samples with low concentration of the element being probed or the samples measured in air or at low energies. In these cases the energy dependence of the background absorption μ_b and air absorption become important.
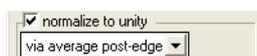
The left picture differs from the right one by added 20 cm of air.

The energy dependent μ_b and air absorption should always be opted. The option 'μ_b is constant' is meant for illustration and for comparison with other programs.

9 Normalization

The normalization, i.e. dividing the spectrum by a constant such that a particular part of the spectrum equals 1, can be done in three different ways: by dividing by (i) the mean value over the specified post-edge region, as on the picture at the right, (ii) the μ value at a particular energy and (iii) the maximum peak value, which was popular some time ago.
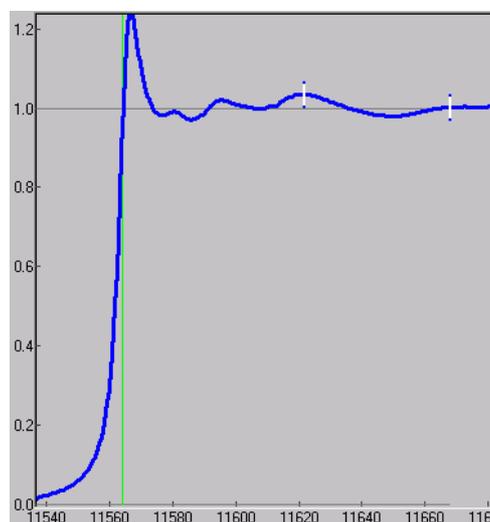
10 Base line subtraction

A base line is needed when considering an absorption peak on a rapidly changing background. There are two ways of how to construct the base line.

10.1 Base line as smoothing spline
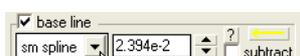
The base line is a smoothing spline drawn through selected regions of experimental points. To make the spline pass under the peak, the peak must be excluded from the spline nodes. The smoothing parameter controls the stiffness of the spline: the bigger the stiffer. The optimum parameter is found visually; there is no good strict criterion for it. This arbitrariness should not make any problem because

normally the smoothing parameter is (visually) good in a very broad range.

to see this example, load the project *Samples/10.1-moallyl-sm-spline.xpj*
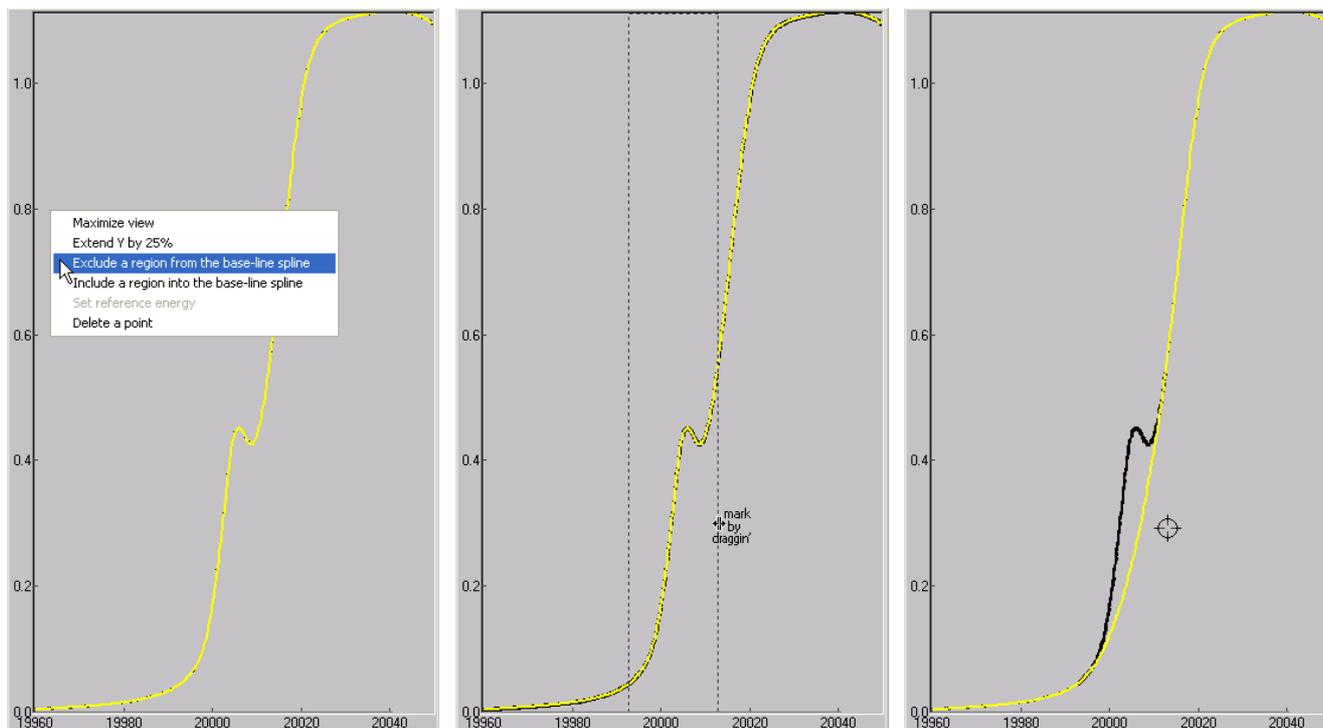
After subtracting the base line with the check box 'subtract', the peak is isolated and can be analyzed for its maximum position (activate the derivative for this), total weight (do integration) or peak fitting.
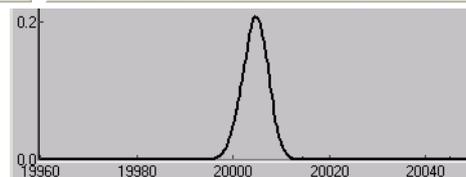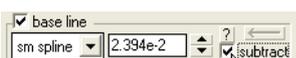
10.2 Base line as spline through adjustable knots
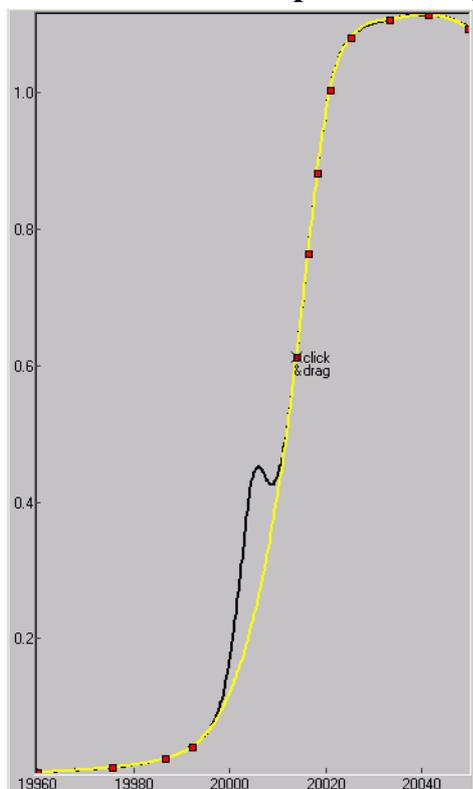
The base line is a spline drawn through the manually put knots. The knot positions can be adjusted by mouse. The knots may be constrained to move only along the μ curve (declare them as 'beads') to facilitate the manual set up.

This method can produce more sophisticated shapes of base lines than the smoothing spline method but requires more time for setting it up.

to see the example at the left, load the project *Samples/10.2-moallyl-knots.xpj*

After subtraction:
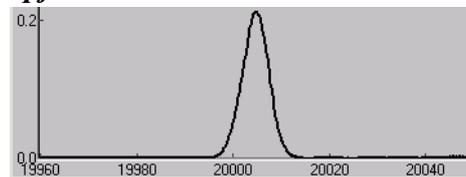
11 Factor analysis

11.1 Principal component analysis (PCA)

PCA was described by many authors. In the XAFS community the mostly cited papers seem to be by Wasserman [1997] (which followed Malinowski [1977]) and by Ressler et al. [2000]. In all the derivations known to me there are two major drawbacks:

1) The PCA test spectra are compared with the data just 'by eye', without statistical grounds for the comparison. Therefore one cannot say how strongly the PCA mismatch may differ from the experimental noise. In other words, not only the mean value is needed for the estimation of noise but also the confidence limits.

2) The experimental errors of different spectra may obviously differ. For instance, reference materials usually have much cleaner spectra than typical diluted samples. Therefore the comparison to noise (or, inversely, the estimation of noise) should be done individually for each spectrum, whereas the standard derivations concern only the global noise.

The original derivation proposed here is free from the above mentioned drawbacks.

Those of you who, like Winnie-the-Pooh are bothered by long words (formulas), go directly to the practical description, Section 11.1.3.

11.1.1 Notation and basic facts

Here, capital letters denote matrices, bold italic letters denote vectors (columns). Notice that $\boldsymbol{a}^T \boldsymbol{b}$ (inner product) is a scalar whereas $\boldsymbol{a}\boldsymbol{b}^T$ (outer product) is a matrix.

A symmetric matrix is fully determined by its eigenvalues and eigenvectors: $A = \sum_j \lambda_j \boldsymbol{e}_j \boldsymbol{e}_j^T$.

The eigenvectors are orthonormal: $\boldsymbol{e}_i^T \boldsymbol{e}_j = \delta_{ij}$. Additionally and less trivially: $\sum_j \boldsymbol{e}_j \boldsymbol{e}_j^T = \boldsymbol{1}$ (unity matrix).

11.1.2 Derivation of PCA based on statistics

From c measured spectra of length r we form an $r \times c$ data matrix $D = [\boldsymbol{d}_1 \boldsymbol{d}_2 \dots \boldsymbol{d}_c]$.

For the covariance matrix $D^T D$ find eigenvalues λ_j and eigenvectors $\boldsymbol{e}_j$ and sort them in descending order in λ's (λ_1 is the largest).

Holds always: $\sum_j^c \boldsymbol{e}_j \boldsymbol{e}_j^T = \boldsymbol{1}$.

If only $M < c$ data vectors are linearly independent, this sum can be truncated at $j = M$ and still $\sum_j^M \boldsymbol{e}_j \boldsymbol{e}_j^T = \boldsymbol{1}$. In this case $\lambda_j \ll \lambda_1 \ \forall j > M$.

In practice the sum is truncated until $D_{PCA} =_{def} D \sum_j^M \boldsymbol{e}_j \boldsymbol{e}_j^T$ coincides with D within noise or, alternatively, the truncated part $D \sum_{j=M+1}^c \boldsymbol{e}_j \boldsymbol{e}_j^T$ remains within noise.

How to compare with noise? Denote the PCA residual $\Delta = D - D_{PCA}$, which must be compared with noise of our data matrix D. Consider
$$\Delta^T \Delta = (\boldsymbol{1} - \sum_k^M \boldsymbol{e}_k \boldsymbol{e}_k^T) D^T D (\boldsymbol{1} - \sum_j^M \boldsymbol{e}_j \boldsymbol{e}_j^T) = D^T D - \sum_j^M \lambda_j \boldsymbol{e}_j \boldsymbol{e}_j^T = \sum_{j=M+1}^c \lambda_j \boldsymbol{e}_j \boldsymbol{e}_j^T$$

We are interested in knowing $(\boldsymbol{d}_i - \boldsymbol{d}_{iPCA})^2$ for each spectrum $\boldsymbol{d}_i$:

$(\boldsymbol{d}_i - \boldsymbol{d}_{iPCA})^2 = (\Delta^T \Delta)_{ii} = \sum_{j=M+1}^c \lambda_j (e_{ji})^2$, where e_{ji} is the i-th component of eigenvector $\boldsymbol{e}_j$.

On the other hand $(\boldsymbol{d}_i - \boldsymbol{d}_{iPCA})^2 / \epsilon_i^2 = \chi_i^2$ if we assume that $\boldsymbol{d}_{iPCA}$ reproduces $\boldsymbol{d}_i$ within noise ϵ_i (*individual noise of spectrum $\boldsymbol{d}_i$*). The variate χ_i^2 must follow the χ^2 distribution law with $\nu = r(c-M)/c$ degrees of freedom. The scaling factor $(c-M)/c$ is due to the fact that $(\boldsymbol{d}_i - \boldsymbol{d}_{iPCA})^2$ is given by $(c-M)$ out of c components. Finally, for the squared noise of spectrum $\boldsymbol{d}_i$ one gets the mean value

$\langle \epsilon_i^2 \rangle = (\boldsymbol{d}_i - \boldsymbol{d}_{iPCA})^2 / \nu = \sum_{j=M+1}^c \lambda_j (e_{ji})^2 / \nu$.

The confidence limits $(\epsilon_i)_{min}$ and $(\epsilon_i)_{max}$ are given by the χ^2 distribution law at selected significance levels. In XANES dactyloscope the significance levels are selected to be 2.5% and 97.5% as to give 95% probability that the measurement noise falls within $[(\epsilon_i)_{min}, (\epsilon_i)_{max}]$ if M out of c spectra are linearly independent.

One can find the *global* noise by averaging $\langle \epsilon_i^2 \rangle$ over all i:

$$\langle \epsilon^2 \rangle = \sum_{j=M+1}^{c} \lambda_j / (\nu\, c),$$

where the normality of eigenvectors was used ($\sum_i^c (e_{ji})^2 = 1$). The last expression is exactly the 'real error' RE introduced by Malinowski [1977]. However, in our derivation we can additionally specify the confidence limits ϵ_{min} and ϵ_{max} in the same way as for the individual noise ϵ_i i.e. by using the statistical properties of χ^2 distribution.

11.1.3 Questions answered by PCA

Unlike the usual descriptions of PCA, the derivation proposed here is capable of answering two direct and two inverse questions:

PCA1) Given the global (average) noise level, how many spectra are linearly independent?

PCA1') How high must be the global noise level in order to have a given number of independent spectra?

PCA2) Given the noise level of a particular spectrum, how many principal components are needed to reproduce the spectrum?

PCA2') How high must be the noise level of a particular spectrum in order to reproduce it by a specified number of principal components?

As you will see in the example in Section 11.1.6 below, the questions PCA1 and PCA2 are not quite the same.

In order to answer the direct questions PCA1 and PCA2 you must know the experimental noise level. How to determine it? See Section 13.

11.1.4 How the PCA results are related to chemical species?

A mechanical mixture of chemical species obviously results in a linear combination of the corresponding spectra. However, if different species have *similar* XANES spectra, the spectra may be linearly dependent even for a set of pure chemical species. The example in Section 11.3.1 illustrates this case. Note therefore that linear dependence of spectra does not necessarily mean mixture of species!

Inversely, if some spectra are distorted due to self-absorption, non-linearity of the fluorescence detector, presence of pin holes etc., linear dependence of spectra may be lost although the samples may really represent mixtures.

Finally, this question should be individually explored in every PCA study. It also involves careful attention to experimental details in order to eliminate systematic distortions.

11.1.5 Is PCA also applicable to EXAFS?

Formally yes, and some people did it, but with very poor logic. EXAFS is described by a sum of modulated sinus functions. Sinus functions form a complete set and as such can be linearly combined to reproduce any function. Thus it is naturally expected that EXAFS spectra are linearly dependent. The 'bad' nature of the EXAFS kernel can also be seen from another side: it is impossible, if without any regularization scheme, to invert the EXAFS equation for getting the radial distribution function. The reason is the same: the degeneracy of the kernel i.e. its low rank when expressed as a matrix of $(2k, r)$ coordinates.

Finally, the functional shape of EXAFS makes one EXAFS spectrum strongly correlate with another one. This correlation happens regardless of spatial structural correlations. Doing conclusions on PCA applied to EXAFS spectra does not substantiate any conclusions on the number of independent structures.

Yet finally, don't do PCA on EXAFS!

### *11.1.6 Usage of PCA in XANES dactyloscope*
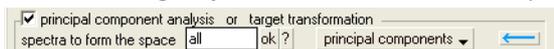
The spectra subject to PCA or target transformation must be defined on the same energy grid. If the grids are different, do the transform (Section 6).

Specify a set of spectra. This is considered either as a data set or as a basis set depending on whether the current spectrum belongs to it. Then, correspondingly, PCA or target transformation is performed.

Load the project ***Samples/11.1-PCA2-dABCnC.xpj*** which has two independent spectra and a spectrum constructed as the average of the two plus normal noise with nominal $\sigma = 0.005$. The thick curves are data and the thin blue ones are the PCA-test curves. The components can be selected/unselected by pressing the button 'principal components'. Unselecting a component means excluding it from the principal ones. As seen, the test curves reproduce the data *exactly* when all the components are selected.
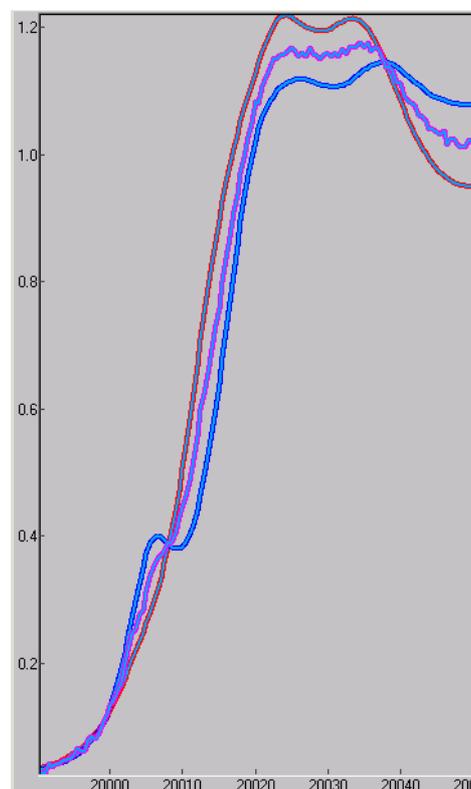

Unselect the last component which is the least important one. As seen on the picture at the right, the spectra are still well reproduced, which is expected as we know that there are two independent spectra and there must be two PC's.
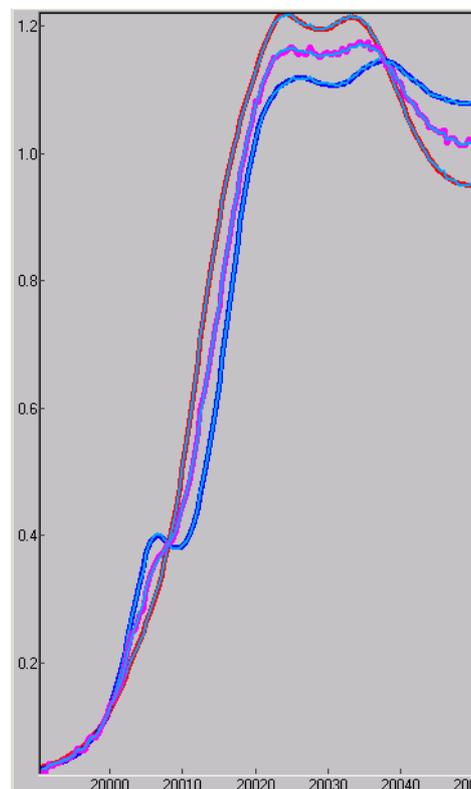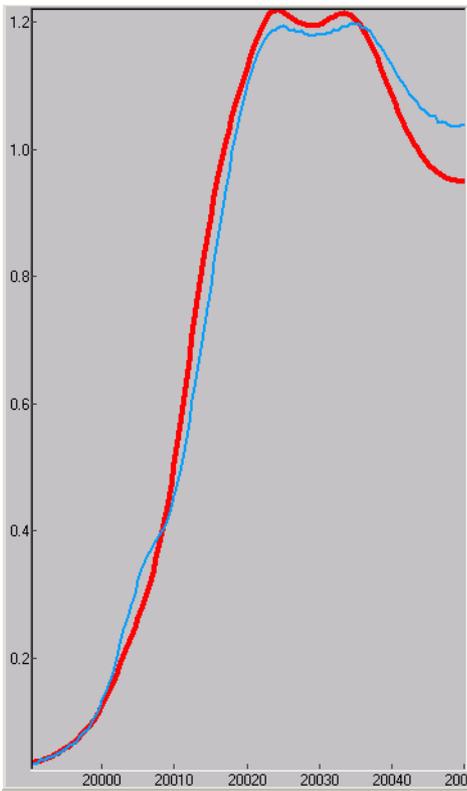
Unselect the second component and see that the first two spectra are reproduced badly ('hide all other spectra' may help in seeing this better), left picture, whereas the third one can surprisingly be reproduced with only one principal component, right picture. This fact shows that some particular spectra may contain less principal components than the number of independent spectra and that the latter figure may be underestimated by visual checking of PCA test. This example shows also *what* is the first principal component in this case: it is the average spectrum.
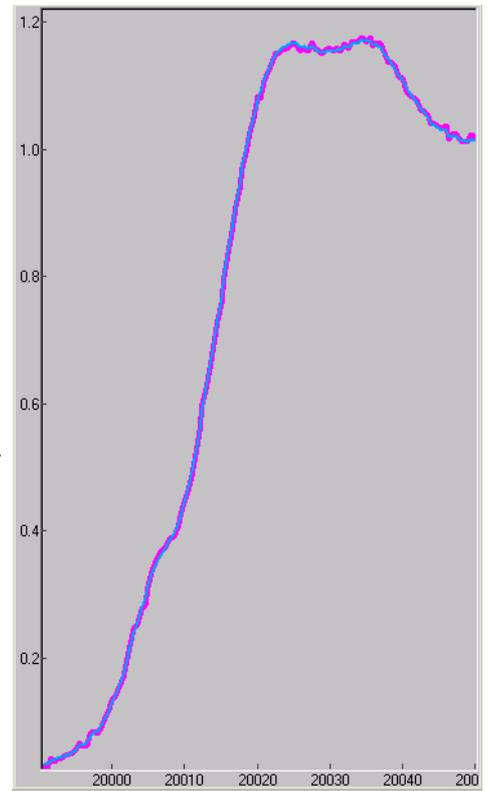
The figures 'ϵ_{min} .. $\langle\epsilon\rangle$ .. ϵ_{max}' reported in the pop-up menu under the button 'principal components' allow to answer the questions listed in Section 11.1.3.

PCA1) *Given the global noise level, how many spectra are linearly independent?* The 'global 95% noise bounds' tell that with 95% of probability the measurement noise must be within the bounds in order to consider the component as unimportant and unselect it from the list of PC's. If your experimental noise is lower then this component must stay selected, if it is higher then there must be some further correlations among the selected components and you should unselect yet more components. Finally, the number of the selected components gives the number of independent spectra. Of course, you do not have to select/unselect the menu items. Just look at the values: where the noise estimations are bigger than the experimental noise, these are the principal components.

PCA1') How high must be the global noise level in order to have a given number of independent spectra? The answer with 95% significance level is in the pop-up menu on one line below the given ordinal number.

PCA2) *Given the noise level of a particular spectrum, how many principal components are needed to reproduce the spectrum?*

for spectrum "1":

The answer, similarly to PCA1, is given by the pop-up menu but in the section 'individual 95% noise bounds'. Notice that these figures are reported only for the current spectrum and generally differ from those for another spectrum, as shown on the left and right pictures.

for spectrum "3":

PCA2') *How high must be the noise level of a particular spectrum in order to reproduce it by a specified number of principal components?*
The answer is similar to PCA1' but in the 'individual …' section. The figures refer to the current spectrum.

In the example above, the artificially added normal noise of σ = 0.005 falls within:
(PCA1) the global noise bounds of the third component, which means *two* principal components;
(PCA2) the individual noise bounds of (a) the second component when the 3rd spectrum is active, which means only one component reproducing the 3rd spectrum; (b) the third component when the 1st or 2nd spectrum is active, which means two components reproducing the 1st and 2nd spectrum.

Let us consider another example:
Samples/11.2-PCA8-(dA1+n)10.xpj. It has 10 spectra which are all artificially constructed from a single spectrum with added 10 various realizations of normal noise of nominal σ = 0.005.

The individual and global noise estimations correctly give only one principal component and the noise level close to 0.005.

The experimental noise level can be found from averaging (see Section 13) as 0.0046.

individual 95% noise bounds

✔ 1: 0.78652 .. 0.88581 .. 1.01403
2: 0.00451 .. 0.00511 .. 0.00589
3: 0.00441 .. 0.00503 .. 0.00586
4: 0.00449 .. 0.00517 .. 0.00608
5: 0.00343 .. 0.00398 .. 0.00476
6: 0.00361 .. 0.00425 .. 0.00518
7: 0.00378 .. 0.00453 .. 0.00566
8: 0.00256 .. 0.00315 .. 0.00409
9: 0.00107 .. 0.00137 .. 0.00190
10: 0.00078 .. 0.00109 .. 0.00180

global 95% noise bounds

✔ 1: 0.78674 .. 0.88606 .. 1.01431
2: 0.00439 .. 0.00497 .. 0.00574
3: 0.00421 .. 0.00481 .. 0.00560
4: 0.00402 .. 0.00463 .. 0.00545
5: 0.00384 .. 0.00446 .. 0.00533
6: 0.00366 .. 0.00431 .. 0.00525
7: 0.00350 .. 0.00420 .. 0.00524
8: 0.00332 .. 0.00408 .. 0.00530
9: 0.00306 .. 0.00391 .. 0.00544
10: 0.00273 .. 0.00381 .. 0.00629
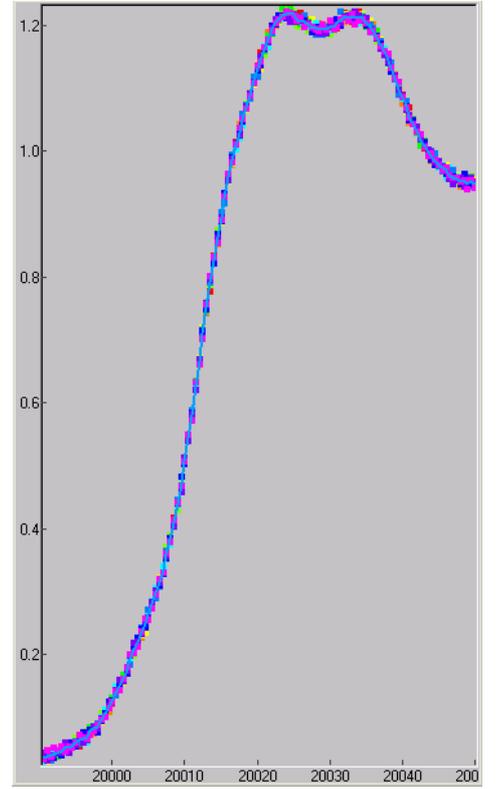
11.2 Target transformation (TT)

You can skip the derivation and go directly to the practical description, Section 11.2.2.

11.2.1 Derivation of TT based on statistics

From c measured basis (reference) spectra of length r we form an $r \times c$ basis matrix $B = [\boldsymbol{b}_1 \boldsymbol{b}_2 ... \boldsymbol{b}_c]$.

If the basis spectra are linearly independent then the covariance matrix $B^T B$ is of rank c and then $(B^T B)^{-1}$ exists.

The matrix $B(B^T B)^{-1} B^T$ is an orthogonal projector to the basis space since it is equal to its square:

$$(B(B^T B)^{-1} B^T)^2 = B(B^T B)^{-1}(B^T B)(B^T B)^{-1} B^T = B(B^T B)^{-1} B^T.$$

Hence, if a spectrum $\boldsymbol{d}$ is a linear combination of the basis spectra then

$$B(B^T B)^{-1} B^T \boldsymbol{d} = \boldsymbol{d} \quad \text{and } \textit{vice versa}.$$

In practice one checks if $B(B^T B)^{-1} B^T \boldsymbol{d}$ coincides with $\boldsymbol{d}$ within noise. The inverse matrix $(B^T B)^{-1}$ is found through the eigenvalues and eigenvectors of $B^T B$ as

$$(B^T B)^{-1} = \sum_j \lambda_j^{-1} \boldsymbol{e}_j \boldsymbol{e}_j^T.$$

This allows to simultaneously do PCA on the basis set in order to check that the basis spectra are independent.

Denote the TT residual $\Delta = \boldsymbol{d} - B(B^T B)^{-1} B^T \boldsymbol{d}$, which must be compared with noise of our spectrum $\boldsymbol{d}$. Taking into account the projector property of $B(B^T B)^{-1} B^T$, we get

$$\Delta^T \Delta = \boldsymbol{d}^T (1 - B(B^T B)^{-1} B^T)(1 - B(B^T B)^{-1} B^T) \boldsymbol{d} = \boldsymbol{d}^T (1 - B(B^T B)^{-1} B^T) \boldsymbol{d}.$$

On the other hand, we represent the spectrum $\boldsymbol{d}$ by a direct sum of the basis spectra B plus a contribution $\boldsymbol{n}$ orthogonal to B:

$$\boldsymbol{d} = B \boldsymbol{b} + \boldsymbol{n},$$

where $\boldsymbol{b}$ is a c-dimensional vector representing the weights of the c basis spectra. Because

$$(1 - B(B^T B)^{-1} B^T) B \boldsymbol{b} = B \boldsymbol{b} - B \boldsymbol{b} = 0,$$

18

and because of orthogonality of $\boldsymbol{n}$ to B, it follows that

$$\Delta^T \Delta = \boldsymbol{n}^T \boldsymbol{n}.$$

Finally, if $\boldsymbol{n}$ is solely due to noise ϵ, the variate $\chi^2 = \Delta^T \Delta / \epsilon^2$ must follow the χ^2 distribution law with $\nu = r - c$ degrees of freedom. Thus the mean value of the squared noise is

$$\langle \epsilon^2 \rangle = \Delta^T \Delta / \nu.$$

The confidence limits ϵ_{min} and ϵ_{max} are found in the same way as in PCA, i.e. by using the statistical properties of χ^2 distribution.

Notice that we cannot use the target transformation method to determine the decomposition weights $\boldsymbol{b}$ because the expression for the experimental squared target transformation residual $\Delta^T \Delta$ does not contain $\boldsymbol{b}$! On the contrary, the squared linear fitting residual $(\boldsymbol{d} - \sum B \boldsymbol{b})^2$ does contain $\boldsymbol{b}$ whence it can be determined.

11.2.2 Questions answered by TT

One direct and one inverse question:

TT1) Given the noise level of a particular spectrum, can the spectrum be reproduced by a linear combination of the basis spectra?

TT1') How high must be the noise level of a particular spectrum in order to reproduce it by a linear combination of the basis spectra?

11.2.3 Usage of TT in XANES dactyloscope

To perform TT of a spectrum, specify a basis set which does not include the target transformed spectrum (the current spectrum).

Note that in TT all the components must be selected. It does not make sense to truncate the sum $(B^T B)^{-1} = \sum_j \lambda_j^{-1} \boldsymbol{e}_j \boldsymbol{e}_j^T$ because the basis spectra are supposed to be linearly independent.

Again load the project **Samples/11.1-PCA2-dABCnC.xpj** which has two independent spectra and a spectrum constructed as the average of the two plus normal noise with σ = 0.005. For the 3rd spectrum active, specify the basis set as '1,2' and see the resulting figures under the button 'target tracking'.

The experimental noise of the target transformed spectrum (here, σ = 0.005) must be within the given noise bounds for the question TT1 be answered positively. If the experimental noise is smaller then there are important contributions which are not inside the basis set. If it is larger (which is unusual) then there are some extra correlations between the basis spectra and the target transformed spectrum, e.g. it is artificially constructed by a linear combination of the basis spectra including their noise.

Check also that the noise estimation of the last principle component of the basis set (here, 0.07393) is much higher than the experimental noise, otherwise the basis set is bad, i.e. internally linearly dependent.
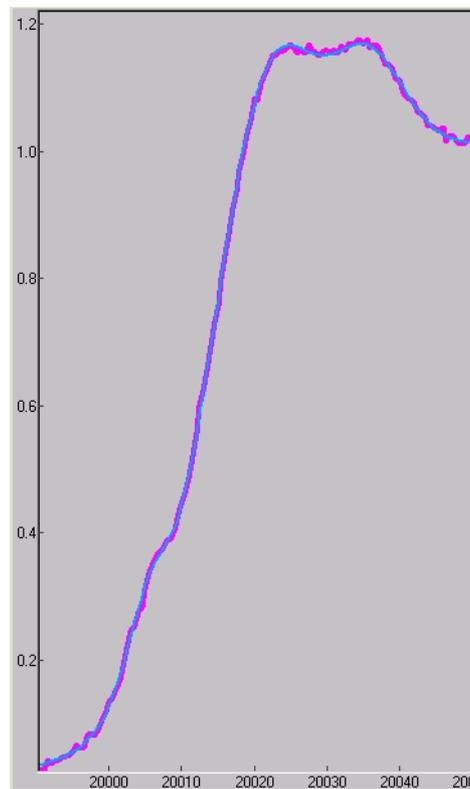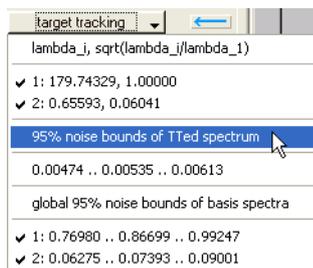
11.3 Pitfalls in factor analysis

11.3.1 Overestimated linear dependence

If different species have similar XANES spectra, the spectra may be linearly dependent even for a set of pure chemical species. To illustrate this, load the project *Samples/11.3-PCA-MoOx.xpj* which has spectra of 6 molybdenum oxides: MoO_2, $Mo_{14}O_{11}$, Mo_5O_{14}, Mo_8O_{23}, $Mo_{18}O_{52}$ and MoO_3. [J. Wienold, T. Ressler, private communication; Ressler et al. 2002]. As seen, there are only 4 or 5 independent spectra out of 6 although each sample has a pure structure as was proven by XRD.

Another example of overestimated linear dependence is given by PCA applied to EXAFS (see Section 11.1.5). EXAFS spectra are usually more linearly dependent than the corresponding spatial structures.

11.3.2 Underestimated linear dependence

Always remember that spectra may have instrumental distortions due to self-absorption, non-linearity of the fluorescence detector, presence of pin holes etc. These distortions may break the linear dependence of spectra even where it would be really expected.

Consider an example of self-absorption from Section 8.3. Load the example project *Samples/08-fe2o3_tr_fl.xpj*. It has 4 spectra of Fe_2O_3 (hematite): measured in transmission and fluorescence, each repeated twice to assure reproducibility. To enable PCA, transform the energy mesh to a new grid with, e.g. 1st node 7080 eV and *dE*=0.5 eV. Apply this transform to all 4 spectra. Switch off the self-absorption correction and activate PCA. As seen in the list of PC's, there are two components with low estimated noise and, hence, there are two PC's, as expected. Now switch on the self-absorption correction again and see that the 3rd component in PCA has quite high noise estimation which does not let neglect it. In other words, the corrected spectrum represents an "independent" species which does not fully merge with the transmission spectra. Inversely, this noise estimation can be taken as the noise level used instead of the experimental noise in the PCA's involving the self-absorption corrected fluorescence spectra of hematite.

In summarizing this example, concentrated references measured in fluorescence must be corrected for self-absorption. Even being corrected, the fluorescence spectra may significantly differ from the transmission ones and thus introduce "new" species into the set of principle components.

11.4 Recommendations for factor analysis

- The reference compounds, as they normally are concentrated, are better to measure in transmission in order to reduce the added uncertainty due to the self-absorption correction.

- All amplitude distortions must be well understood and prevented/corrected.

- It always makes sense measuring a calibrated test mixture.

12 Fitting by user-defined formula

The primary usage of this section is doing a linear combination fitting after the factor analysis.

The fitting formula is typed in by the user. It operates the letters 'a' through 'y' ('E' stands for energy as independent variable; it is internally renamed to 'z') and 'any' usual mathematical operations and functions. A letter can be declared as a fitting parameter or a spectrum loaded by XD. In the latter case its energy shift may vary as an additional fitting parameter. This capability can be useful when the energy axis is not well reproducible or when mixing data from various beamlines or, as in the example below, when modeling different spectral features by a single contribution.

Load the project *Samples/12-cefit34.xpj* which has a Ce L3 XANES (spectrum #2, red) fitted by a weighted sum of monovalent 3+ and 4+ contributions. The "3+" spectrum was calculated by FEFF (spectrum #1, black). The "4+" contribution is represented by the same calculated spectrum shifted by a fitting value to higher energies.

Thus the experimental spectrum is fitted by the formula 'a+b*c', where 'a' and 'b' are the same shifted spectrum #1 (the black curve), 'c' is a scalar:
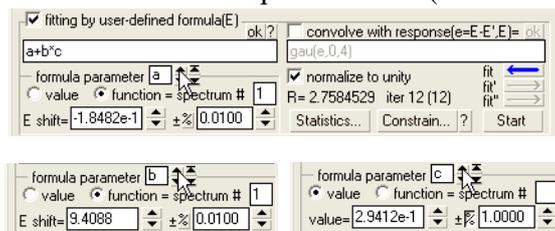
The average valence is given in this case by $[(3+)+(4+)\cdot c]/(1+c)$.

After the automatic fitting has finished, press 'Statistics...' button. You should select the 'integrated' option for the errors (δ's) of the fitting parameters. See VIPER manual for the description of the other options and the methods behind. See VIPER manual for the description of the statistical χ^2 and F-tests.

The colored matrix shows the pair-correlation coefficients. Completely red and blue denote +1 and −1, black is 0. The fitting errors are listed at the left of the correlation matrix. Pay attention to the correlation coefficients. They should not be close to +1 or −1 or, visually, much colored or, when displayed by the correlation map (the yellow-black graph), diagonally stretched. This would mean large fitting errors and frustration for the minimization algorithm. In this case try to apply constraints to the fitting parameters using the button 'Constrain...'. Alternatively, one can fix a fitting parameter by setting its initial increment to zero.
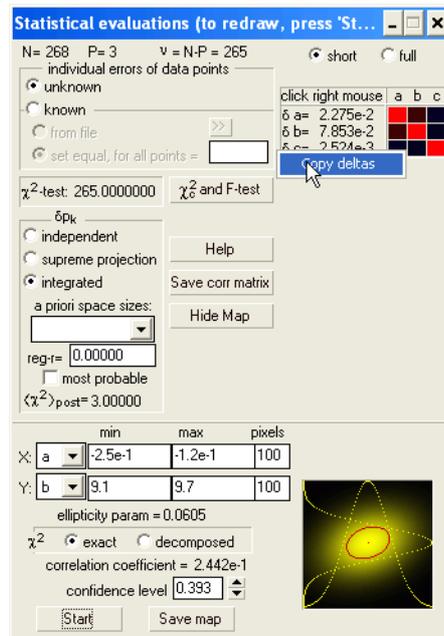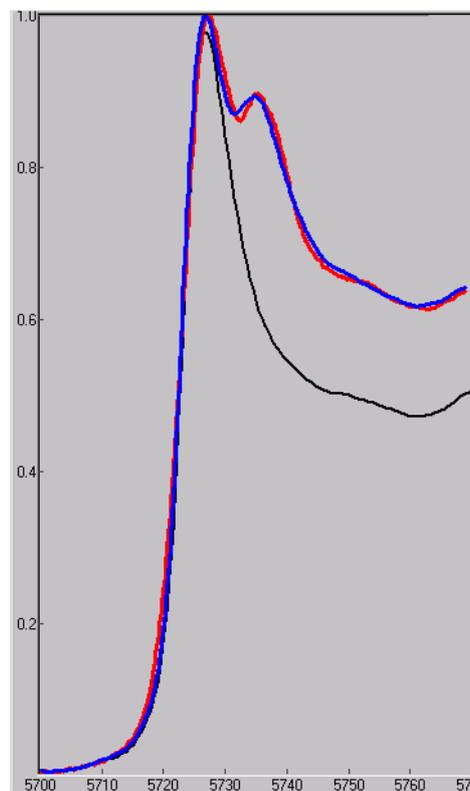

13 Creating average, rms and difference spectra

Average, rms and difference spectra can be added via 'Spectra' menu:

Such spectra, called 'special' in XD, are updated whenever the original spectra from which the special spectra were constructed have changed.

Here you can average several repetitions of one spectrum and/or several fluorescence spectra measured by a multi-pixel detector.

An rms spectrum is useful for determining the experimental noise. Load the project: ***Samples/11.2-PCA8-(dA1+n)10.xpj***. It has 10 spectra which are all artificially constructed from a single spectrum with added 10 various realizations of normal noise of nominal σ = 0.005. Create an rms spectrum and make it active. In the description line at the top of the main dialog window find the mean value of the rms spectrum. This value can further be used in factor analysis or in calculating the fitting errors.
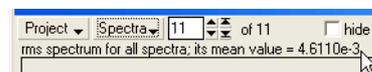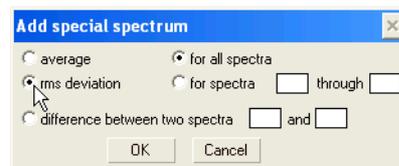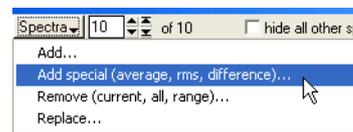
14 Exporting data and saving project file

The curves visible in the main graph window can be exported to a column file, use 'Project/Make output file...'.

Another very useful function of XD is saving project files. A project file has description of data files and all the processing steps. The project files Samples/*.xpj have been saved in this way.

Important: Project files are text file. You can edit them by any common editor. A newly created project file has full path references to the data files. If you move the data files or if you want to load the project on another computer, you should change the paths accordingly. I normally keep project files in the same directory with data. Then I keep only the file names in a project file and manually delete the directory paths by Search/Replace command in a text editor.
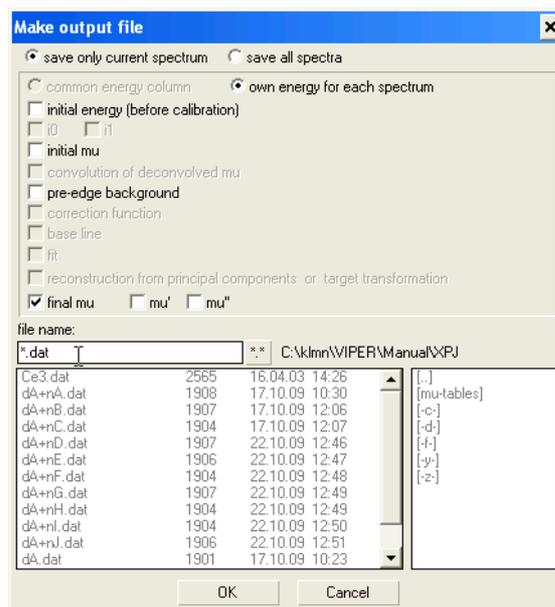
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