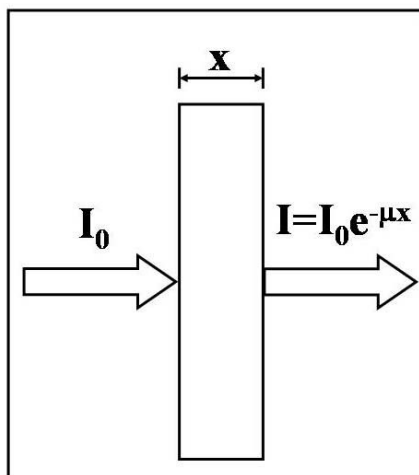**Transmission mode: Sample preparation for XAS**

1) <u>Physical principles</u>

In transmission mode we are measuring the attenuation of the X-ray beam as it traverses a sample of thickness *x*:

$$I(E) = I_0(E)e^{-\mu(E)\cdot x}$$

where I_0 and I are the intensity of the incident and transmitted X-ray beam, respectively, and μ is the absorption coefficient. In turn, μ depends on the atomic concentration (ρ) and absorption cross-section (σ):

$$\mu = \rho \cdot \sigma$$

For a sample consisting of different atoms, the total absorption will be given by the sum of the product for each chemical element present in the sample:

$$\mu_{tot}(E) = \sum_i \rho_i \cdot \sigma_i(E)$$

The cross section is a physical property of the element, i.e. a constant (you can find the tabulated values at http://csrri.iit.edu/periodic-table.html). As such, the way you prepare your sample would affect the absorption coefficient through the atomic concentration (ρ_i).

Two aspects have to be considered: the *total absorption* and the *edge jump* for the element of interest.

The total absorption of the sample should be such that you have enough transmission through the sample to get a decent signal for the X-ray beam after the sample (i.e. in the second ion chamber, *I*).

A correct edge jump ($\Delta\mu \cdot x = (\mu(E_2) - \mu(E_1)) \cdot x \approx 1$, where E_2 and E_1 are the energies above and under the edge, respectively) assures that you can acquire a XAS signal good enough to be analyzed. This is achieved only if the element of interest is a major component because the difference of the absorption coefficient above and under the edge is mainly due to the change in the cross section of the investigated element. In the event the sample is too dilute (by element of interest) you will not be able to acquire a good spectrum because

your edge jump will not be big enough even if you obtain the correct value for the *total* absorption. Adding more product will not help to solve the problem in this case, rather you will need to explore doing the measurement in fluorescence mode.

2) <u>Which kind of sample do I need?</u>

The state of the sample is not particularly important for XAS measurements (it can be a powder, foil, film, amorphous) since this technique probes the local structure around the absorber (no need for a long range ordering). However, certain homogeneity is required.

XAS is a selective technique so you do not have to worry about the presence of other chemical elements in your samples (unless their edges interfere with the investigated edge) but you have to be absolutely confident that your sample does not contain impurities of the investigated chemical element. This is because XAS probes an average local structure around the absorbers.

The most common way to prepare solid samples is to make pellets. For this you will need:

- The right amount of sample powder fine grained and homogeneous (see next section).
- A binding/briquetting agent (cellulose is preferred) to add to your sample powder. The agent is added in order to make the pellet more stable and to reach a quantity of total product which is enough make the pellet. For a pellet of approximately 1 cm^2 we suggest to use about 100 mg of binding agent.
- A die set and a hydraulic press (see below: '*How to make a pellet*').

3) <u>Estimating the right mixture</u>

In order to calculate properly the quantities necessary for your sample preparation we recommend the use the *XAFSmass* program (if you want to go with first principles, see the last page):

http://www.synchrotron.org.au/index.php/aussyncbeamlines/x-ray-absorption-spectroscopy/publications-and-resources

Calculations for different applications are available in this program. However, the most common applications are: - <u>the calculation of the quantity (in mg) of powder needed to prepare samples with an optimal absorption for transmission measurements</u> and - <u>the calculation of thickness and absorption step for samples with known density</u>.

- **calculation of the quantity (in mg) of powder needed to prepare samples with an optimal absorption for transmission measurements.**

This utility helps you to calculate the quantity (in mg) of powder provided you know:

1) Sample chemical formula

2) Desired total absorption above the edge (we suggest to adjust this value to be between 1 and 2 and such that the 'absorptance step' calculated by the program would be close to 1)
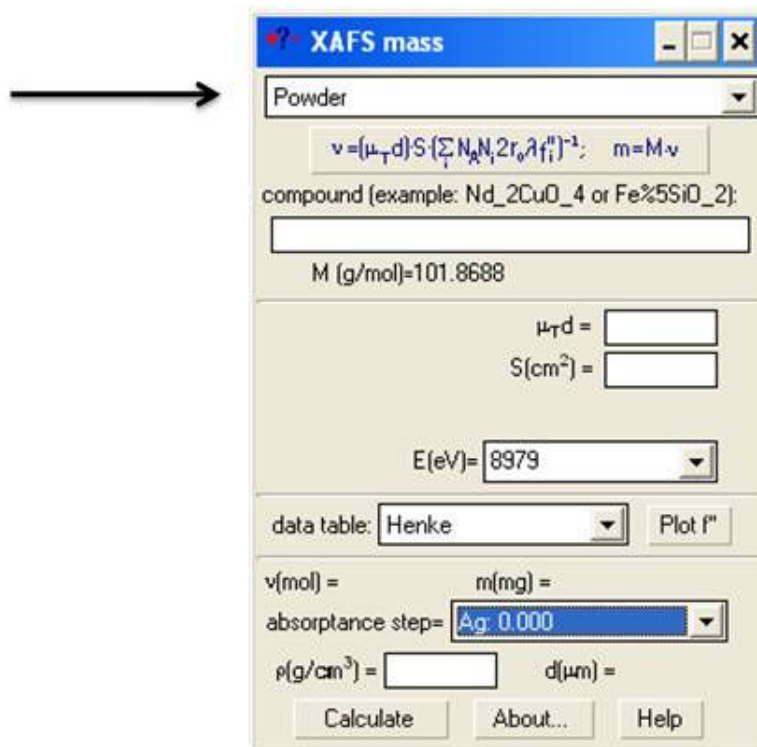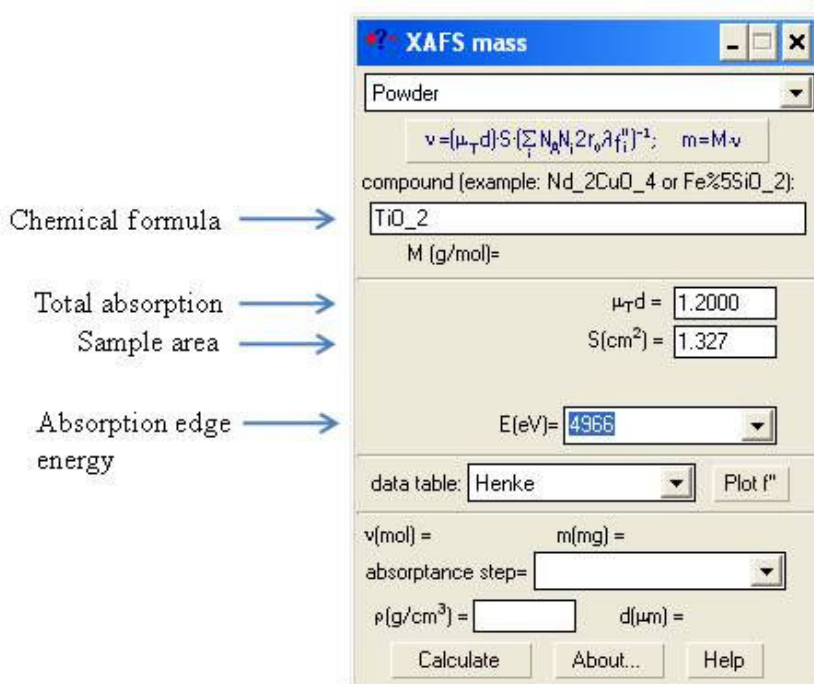
3) Sample area

4) Absorption edge energy

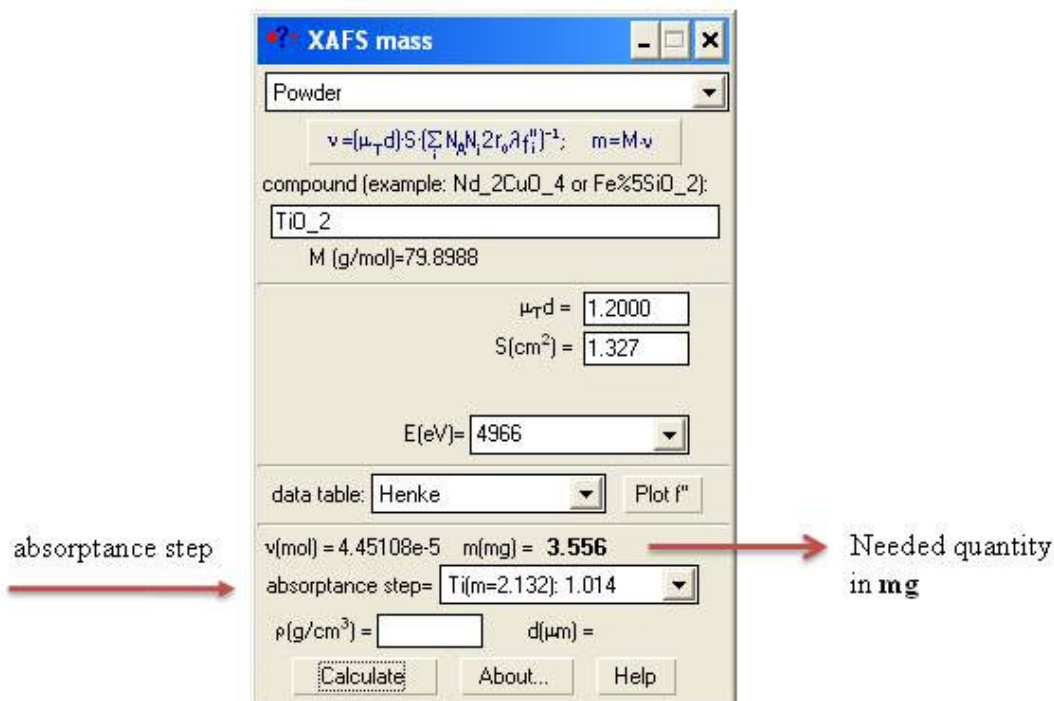- Select 'powder' from the main menu:

- Type the chemical formula, the desired total absorption, the sample area (this would depend on the die of your hydraulic press) and the edge energy of the absorption edge.

- Press calculate and you can have the needed quantity in mg.

absorptance step →

Needed quantity in **mg**

This utility also allows you to calculate the absorptance step for an atom which is substituted in a given percentage in your product. For example if you want the Fe edge in SiO_2 with 5 % in weight of Fe you should write in your chemical formula Fe%5SiO_2. Remember that the percentage is given in *weight*. If you have the atomic percentage than you should use this conversion:

Wt % = at % * (atomic weight of the chemical element/molecular weight)

4) How to make a pellet

1) Ascertain the amount of quantity of powder you need to prepare your sample.

2) Mix your powder sample with a binding agent in a mortar. We suggest to use cellulose (boron nitride diffracts). Ascertain that the two products are homogeneously mixed (use a mortar and pestle or a mini-ball mill).

3) Use the mechanical auto press or the handheld press (see pictures below). The auto press is located in the chemistry lab, the handheld press is located in the XAS sample mounting area (please use it in the chem. lab. and return after use to the beamline cabin). A manual is available for the auto press in the chem. lab.

Soil + Cellulose pellet

APPENDIX – First principles for calculating sample quantity

Here is what you need:

$$I = I_0 e^{-\mu_{tot}(E)x}$$

where E is the energy above the edge.

$$\mu_{tot}(E) \cdot x = desired\ total\ absorption\ (fixed)$$

$$\mu_{tot}(E) \cdot x = \sum_i \frac{N_i}{V} \sigma_i(E) \cdot x = \left(\sum_i n_i\, \sigma_i(E)\right) \cdot \frac{N_{molecules}}{V} \cdot x$$

where N_i are the total number of atoms of the chemical element i and n_i are the number of atoms of the chemical element i contained in one molecule of your product.

$$= \left(\sum_i n_i\, \sigma_i(E)\right) \cdot \left(\frac{N_{moles} \cdot N_A}{V}\right) \cdot x$$

$$= \left(\sum_i n_i\, \sigma_i(E)\right) \cdot \left[\frac{weight\ in\ g}{molecular\ weight} \cdot \frac{1}{V} \cdot N_A\right] x$$

$$= \left(\sum_i n_i\, \sigma_i(E)\right) \cdot \left[\frac{weight\ in\ g}{molecular\ weight} \cdot \frac{x}{S \cdot x} \cdot N_A\right].$$

where S is the sample area that you provide, n_i and molecular weight are calculated according to the chemical formula you provide, the cross sections σ_i are tabulated (see 'data table') and N_A is Avogadro's number. So you have everything to calculate the needed weight.

These calculations are performed above the absorbing edge. Then the edge jump is calculated as

$$\Delta\mu_{tot}(E) \cdot x = (\mu_{tot}(E_2) - \mu_{tot}(E_1)) \cdot x =$$

$$\left[\sum_i n_i\, [\sigma_i(E_2) - \sigma_i(E_1)]\right] \cdot \left[\frac{weight\ in\ g}{molecular\ weight} \cdot \frac{x}{S \cdot x} \cdot N_A\right].$$