

SAMPLE PREPARATION:



1



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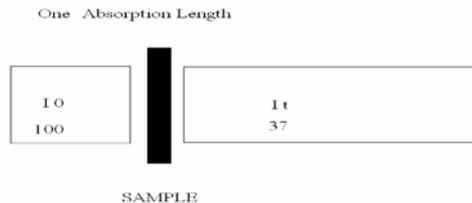
Nov 14, 2014

Things to consider before making the sample

- What XAS method to be used?
 - Transmission
 - Fluorescence
 - Electron Yield
- Amount of sample one needs ? Kind of sample
- How to prepare the sample?
- Elements in the sample we are dealing with-close absorption edges?-Many Ks and L edges overlap or they are within K value of < 10 , difficult for analysis.
- **FOR TRANSMISSION:**
 - The rule of thumb is that if the content of the element of interest is one weight % or more, you are better off doing XAS in transmission. (Could be 5 % or more difference of opinion. TRY IT).
 - Be careful what are the other elements in the sample.
 - The other criteria is the edge jump is $>$ or $= 0.1$ (absorption length difference above and below the edge.

Absorption Length

- Absorption Length: A useful term to know.
- $\ln(I_0 / I_t) = \mu x = 1$, then the thickness of the sample $x =$ one absorption length
- It is same as $I_0 = e \cdot I_t$, or $I_0 = 2.718 \cdot I_t$
- In other words, I_t becomes 37% of I_0 .



- **Rule of 10**
microns i
e.g Cu K-edge = 8.979 KeV, One Absorption length ~ 9 micron.
- elements: One Absorption length in edge in KeV.

How big is a micron? How big is a nano meter?

SAMPLE THICKNESS:

- Pure elements are useful as reference when doing EXAFS but not that much fun.

The Gurus of XAS suggest a good absorption length of 1-3 for the samples.
Mostly samples are not single elements: Real samples as well as standards.

- Following formula should be used to find the amount of sample we need:

In transmission mode.

$$Wd = \ln(I_0/I_t) / \sum\{(\mu/\rho)_j \cdot w_j\}$$

Wd = mass of the sample in g / cm²

μ/ρ = total cross section (absorption coefficient / density) of element 'j' above the absorption edge of the EXAFS element under study in cm²/ g

w = weight fraction of element j in the sample

- The sum is over all the elements in the sample including the EXAFS element.
- The value “ $\ln(I_0/I_t)$ ” is 1-3 in most of the calculations.

http://www.csrri.iit.edu/mucal.html

Mucal on the web - Windows Internet Explorer

http://www.csrri.iit.edu/mucal.html

File Edit View Favorites Tools Help

Mucal on the web

Mucal on the web

This is a program to calculate x-ray absorption coefficients. It uses the fortran subroutine mucal written by Pathikrit Bandyopadhyay. You can get the original subroutine (mucal.f and a c version, mucal.c) [here](#).

If you want to know edge energies, fluorescence yield, etc. of an element fill in the symbol and submit query. For x-ray absorption coefficients, also fill in the energy of interest in the energy box.

Element Symbol:

Energy: keV - Please note that values above 500 will be treated as eV rather than keV

To submit the query, press:

Calculations are based on data compiled By *W. H.McMaster et. al.*

Fluorescence yield data by *M. O. Krause, J. Phys. Chem. Ref. Data. 8, 307(1979).*

Please report problems to [Carlo Segre \(segre@iit.edu\)](mailto:segre@iit.edu).

start Microsoft PowerPoint ... http://gbxafs.iit.edu/... Mucal on the web - W... Internet 100% 2:47 PM

Answer from McMaster Table:

X-ray properties

Data for Cu; Z = 29 atomic weight = 63.5400009; density = 8.93999958

K-edge at: 8.97900009 keV

L-edges at: 1.10000002, 0.952000022, 0.931999981 keV

M-edge at: 0.119999997 keV

K-Alpha1,K-Beta1 at: 8.04699993 8.90400028 keV

L-Alpha1,L-Beta1 at: 0. 0. keV

K,L1,L2,L3 jumps: 7.95528412 1.15726078 1.40999997 2.87400007

Fluorescence yield for K,L1,L2,L3: 0.4400, 0.0016, 0.0100, 0.0110

Cross-sections at E = 9. keV Photoelectric 285.486938 cm²/gm

Coherent 1.70745862 cm²/gm

Incoherent 0.0718918592 cm²/gm

Total 287.266266 cm²/gm

The unit conversion factor (C) is 105.5 {(Barns/Atom) = C * (cm²/gm)}

Absorption coefficient 2568.1604 1/cm

1/mu (element): 3.89383793 microns

Created by Pathikrit Bandyopadhyay, recent updates by Carlo Segre. Calculations are based on data compiled By W. H.McMaster et. al.

Fluorescence yield data by M. O. Krause, J. Phys. Chem. Ref. Data. 8, 307(1979).

Please report problems to Carlo Segre(segred@iit.edu).

Fe₃O₄ (magnetite) at 7.2 KeV

<http://www.csrri.iit.edu/periodic-table.html>

Density of magnetite 5.2 g / cm³

MW=3 X 55.9 g / mol + 4 x 16.0 g / mol = 231.7 g / mol

Cf = Total cross section of Fe at 7.2 KeV = 393.5 cm² / g-----→ From cross section tables

Co = Total cross section of O at 7.2 KeV = 15 cm² / g -----→ From cross section tables

wf = Weight fraction of Fe in Fe₃O₄ = 3 x 55.9/231.7 = 0 .724

wo = Weight fraction of O in Fe₃O₄ = 4 X 16.0 / 231.7 = 0.276

μ = density (cf x wf + Co x wo) = 5.2 (393.5 x 0.724 + 15 x 0.276)

= 1503/cm = .15/micron

Absorption Length = 1 μ m/.15 = 6.7 microns

Uniform Sample Thickness:

Brick and Hole Effect:

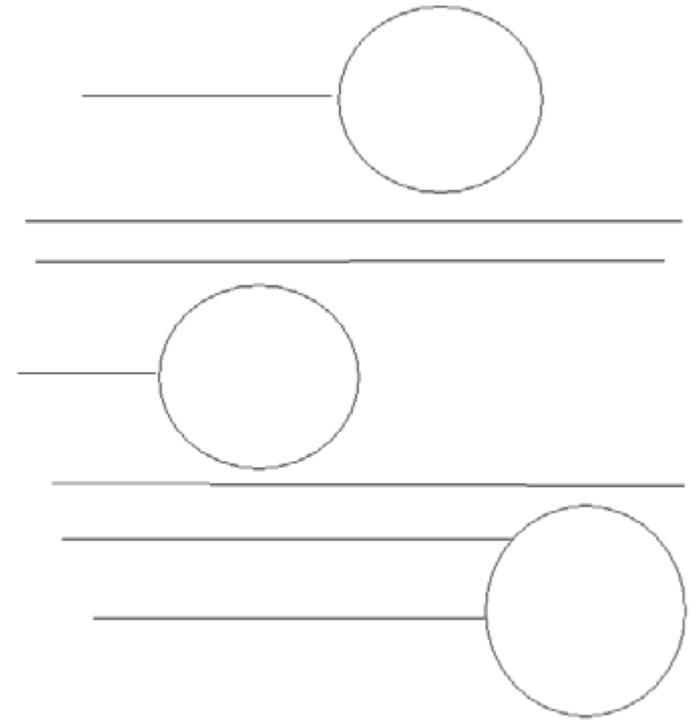
Best Sieve: 600 mesh, meaning in one inch square there are 600 x 600 holes

.
The size of particles we get from it = $25400 \text{ micron} / 1200 \sim 21 \text{ micron}$.

Too big a particle size for most of the EXAFS work.

What if the particles are 100 Angstrom?

Suggestion: Particle size much less than absorption length.



Use Sieve and Mortar and Pestle:

Grind the sample as good as you can. Sieve it before grinding.

Brush the finest particles on a 6 inch scotch or Kepton tape. Tap the back of the tape so that large particles will come out of it. This can also be brushed.

As a result you expect to have particles of the order of around 5 microns left on the tape.

This tape can be folded to 4-6 folds to minimize the holes effect.

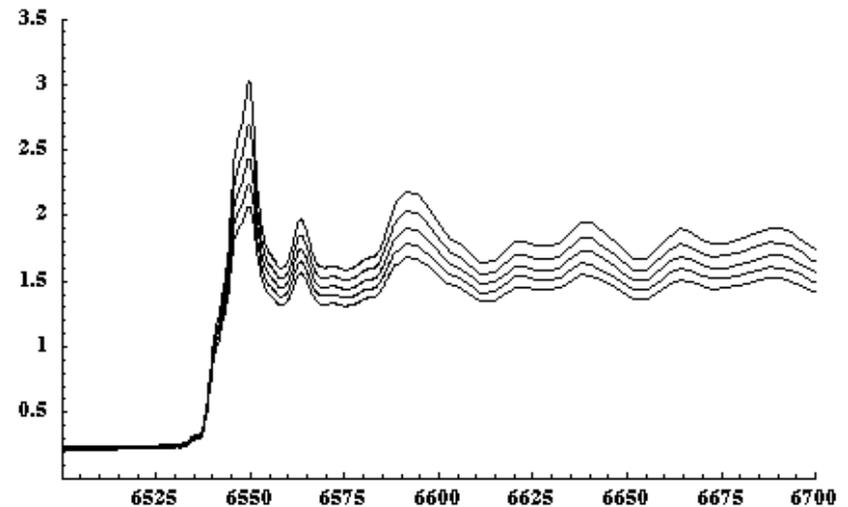


Effect of non-uniform sample

Effect of Gaussian Thickness

Effect of leakage (pin holes)

Effect of harmonics. What is it?



They all contribute to distort the Real value of μ_X

Compare with published data?

MnO 10 micron thick

~2 absorption lengths

leakage varied from 0% to 10%

Edge jump is reduced

EXAFS amplitudes are reduced

white line height compressed

thickness effects distort both XANES

and EXAFS - screw up fits and

integrals of peak areas

If you are fitting XANES spectra, (Grant Bunker)

SAMPLES FOR FLUORESCENCE MODE

It is preferable to make samples in transmission mode, briefly, taking all precautions, like particle size less than absorption length, avoid brick and hole effects, uniform samples, harmonic minimized beam, absorption length > 0.1 etc.

If these conditions are not met and there are many situations that they will not meet.

Answer is to try in fluorescence mode.

That creates many other problems:

Loss of signal photons: We do not collect 4π

Keeping sample at 45 degrees? Scattering : Fluorescence ratio

Self Absorption effects: Nothing comes out from big particles

Thin concentrated sample: EXAFS equation holds-search for mathematical details

Thick dilute sample: EXAFS equation holds-search for mathematical details

Fluorescence Efficiency: All incident photons will not produce fluorescent photons

Each particle size still smaller than absorption length: $x=0.1$ to 8

Still need uniform and flat surfaces.

CORRECTIONS:

The particle size has similar effect on the spectra as shown in the graph.

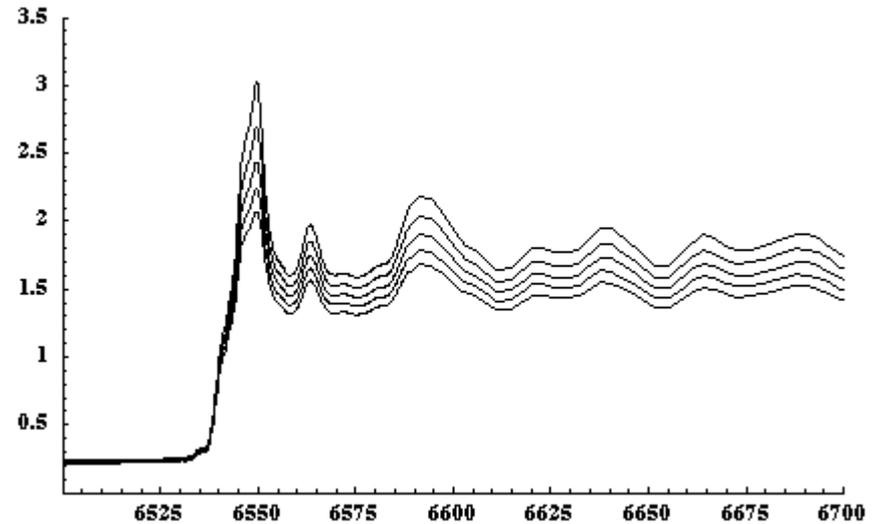
Could make XANES analysis trouble some

If the particle size is not small then even the shape and orientation of the particles can affect the quality of data.

However, all is not lost, there are many mathematical models and corrections are available, for example in case of a thick and concentrated sample. (Grant Bunker Tutorial)

Best is to avoid that situation:

Report in the publication how the sample was prepared.
expected particle size, absorption length of the sample etc.



XAS USING ELECTRON YIELD TECHNIQUE:

When a core hole electron is knocked out, outer electron takes its place. The energy released some times knocks out another electron, called Auger electron. The electron ionizes the He gas in the chamber, and signal is produced.

The effect produces EXAFS spectrum, just like XAS in fluorescence.

CAUTION:

Electrons penetration depth is small, about 100 nm, so cannot be used for bulk samples. Ideal for surface structures.

The sample has to be mounted on a conducting material.



Practicle Step by Step Procedure to make samples:

1. Find absorption length of the sample above the edge of element of interest. Mostly comes out to be in few microns.
2. If using g/cm^2 formula then mostly comes in few 10s of mg
3. Take few 100 mg of sample. Using mortar-pestle, ball mill, grind it, sieve it, grind again. Sieves range from 100 – 600 mesh, still particles about 20 micron. Do not heat, could change state, or aggregate. Keep grinding....
4. Use sedimentation technique for few micron size particles. (next slide)
5. In step 3, add binders like BN, BC, graphite, sugar etc. (impurity free), only if making pellets, and the amount of sample is very small from steps 1, 2.
6. Take 5-7 inch of thin scotch or Kepton tape, uniformly spread the step 3 sample on it, brush it, or with fingers spread it. Tap the tape to get rid of larger particles. Make 4-6 folds to minimize pin holes.
7. Check the quality of samples by all means available: Optical spectroscopy-absorption Particle size analyzer, microscope, electron microscope etc.

SEDIMENTATION:

$$T = 9/5 \times nh / (p-p_0) g R^2$$

T = sedimentation time

n = viscosity of the liquid e.g for acetone it is = .0032 g / cm x S at 20 deg C

h = height of the liquid column e.g = 5 cm

p = density of the particle e.g MnO = 5.4 g / cm³

p₀ = density of the liquid e.g acetone = 0.79 g / cm³

g = acceleration due to gravity = 980 cm / s²

R = radius of particles required e.g we need one micron size.

T = 638 seconds

In this time one micron particles will settle down.

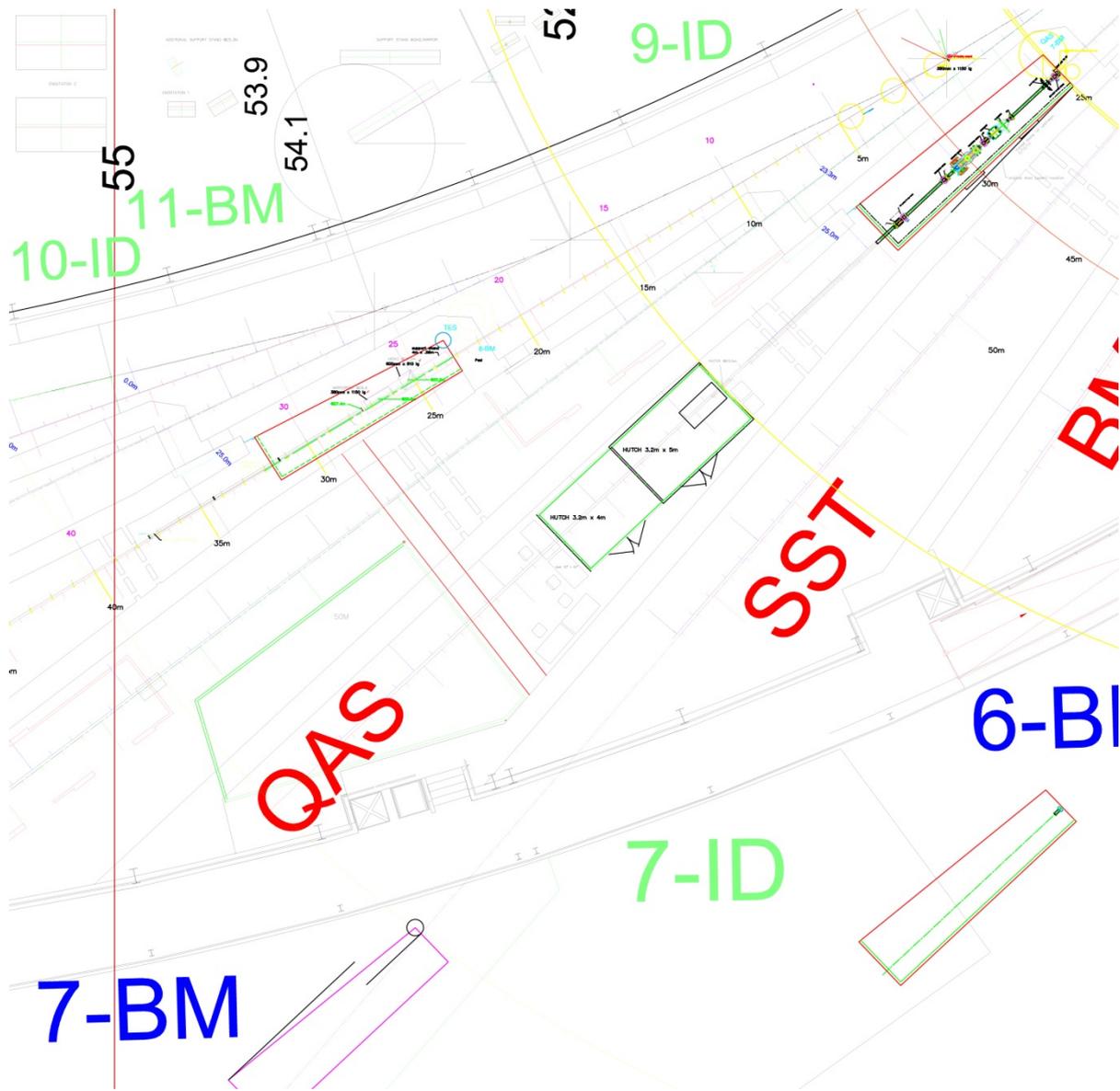
Using pipette take out the supernatant liquid.

Dry the samples, and now you have required size particles.

Grant Bunker's Tutorials.

SUMMARY:

- Make sure the beam is uniform. Right width and right height for energy resolution.
- Using X-Z translation stage, scan in both directions, use the most uniform part of sample.
- Make sure about total beam goes through I0, through sample and through It, also If.
- Change the orientation of the sample for better uniformity.
- For glancing angle, use glancing angle slides to maximize surface area, if sample on surface.
- If crystalline sample or substrate, rotate the sample.
- Cool down the sample using liquid nitrogen or displex-cryostat system for better quality.
- For low Z elements < 3 KeV, use He purged chambers, or vacuum if possible.
- For liquids and gases use special cells or sample holders to trap the sample.
- In fluorescence, always measure a blank sample-make sure it is free from element of interest



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Thank you