

# MATERIALS CHARACTERIZATION FUNDAMENTALS



*Franklin & Marchall College*

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# Materials Characterization Fundamentals

Franklin & Marchall College

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## Licensing

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A detailed breakdown of this resource's licensing can be found in [Back Matter/Detailed Licensing](#).

## CHAPTER OVERVIEW

### Diffraction Techniques

Crystal structure basics

Electron Diffraction

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X-ray diffraction (XRD) basics and application

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## Crystal structure basics

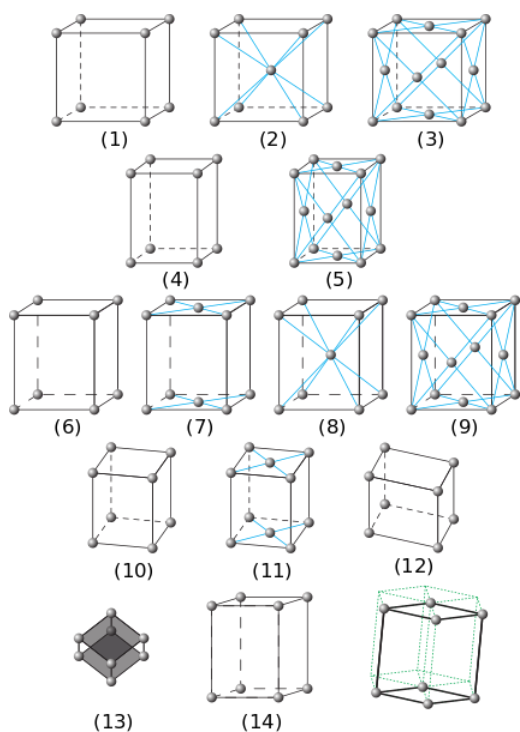
Student authors: Jason Stott & Victoria Bublin 2020

### Describing crystal structures

#### Unit cells and lattice types

To understand the properties of a crystalline solid, one must first understand the structure. The most useful way to describe the structure of a crystalline solid is by breaking it down into its smallest repeating unit, known as the **unit cell**. The unit cell is repeated infinitely in all directions in the theoretical bulk crystal solid. A unit cell is described by lattice points, which together make up various **lattice types**. A unit cell can also be described using dimensions of length, width, and height. The different lattice types can be differentiated by their dimensions as well as the placement of atoms within the cell. There are 14 different lattice types.

<https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch13/unitcell.php>



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1. Cubic P
2. Cubic I
3. Cubic F
4. Tetragonal P
5. Tetragonal I
6. Orthorhombic P
7. Orthorhombic C
8. Orthorhombic I
9. Orthorhombic F
10. Monoclinic P
11. Monoclinic C
12. Triclinic
13. Rhomboedral
14. Hexagonal

Ions within the crystal lattice can be located using a three number coordinate system. For example, (0,0,0) indicates an ion on the origin, and (1,1,1) indicates an ion that is one unit away from the origin in the x, y, and z directions. Edge cells must be equivalent, so an ion on the origin implies one at each corner. Different lattice types have different efficiencies or densities. This means that some unit cells contain more “full molecules” than others. Those containing more full ions are considered more efficient.

### Miller indices

### Wyckoff positions

- Where atoms can be found in a general structure. Often paired with space groups these are the gaps in the crystal structure that can be occupied. This gives vital information to the structure and the kind of arrangements
- This gives more information about the and how other atoms fit in the nanostructure. Knowing this can tell a lot about the reactivity as well as other properties such as photoluminescence.
- <https://pubs.acs.org/doi/10.1021/acs.inorgchem.5b01510>
- [https://www.cryst.ehu.es/cryst/get\\_wp.html](https://www.cryst.ehu.es/cryst/get_wp.html)

### Space groups

- This tells us the general form of the crystal and how we can categorize its symmetry and shape. A given spacegroup gives all information about the surfaces
- Reading this tells us the morphology of the structure which could effect reactivity as well as other properties.
- <https://pubs.acs.org/doi/10.1021/acsomega.9b04012>
- [https://www.britannica.com/science/space-](https://www.britannica.com/science/space-group)  
[group,http://img.chem.ucl.ac.uk/sgp/large/sgp.htm](http://img.chem.ucl.ac.uk/sgp/large/sgp.htm),<https://journals.aps.org/pr/abstract/10.1103/PhysRev.96.280>

### Good literature examples

<https://science.sciencemag.org/content/293/5532/1123>

### Further reading

<https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch13/unitcell.php>

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## Electron Diffraction

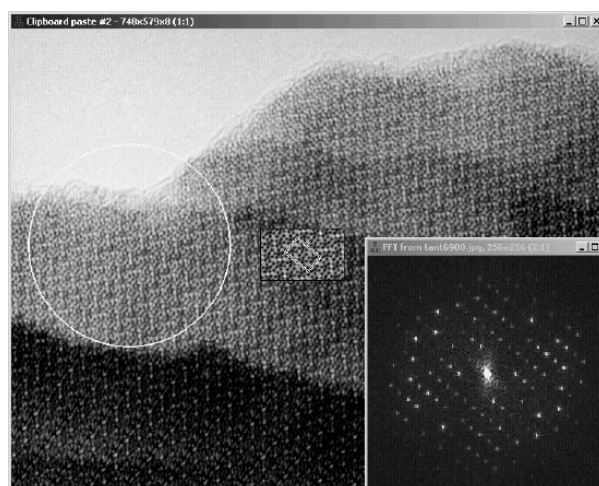
Student authors: Mint Pungsrjai 2019

Electron diffraction technique utilizes the wave nature of electron in studying the crystal structure of the sample of interest in terms of chemical positions and nanoscale's atomic positions with high precision. This technique studies the phenomenon of the diffraction pattern resulting from the interference of a beam of electrons and the crystalline materials. The technique is usually performed in a transmitting electron microscope (TEM), and scanning electron microscope (SEM) as electron backscatter diffraction.

### How electron diffraction works

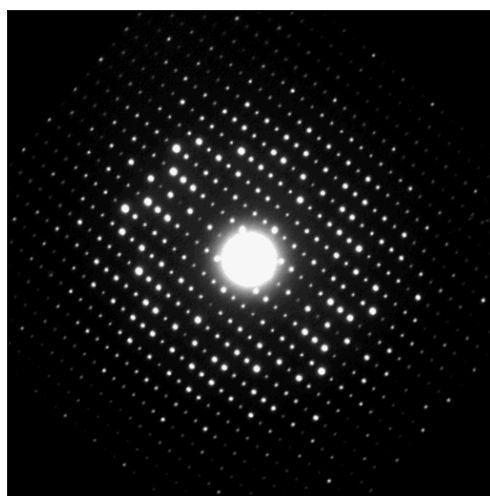
The sample requires to be really thin so that it is transparent to electrons. In the instrument, electrons are accelerated in order to create an electron beam consisting of high-speed electrons with a short and known wavelength that is comparable to the spacing in the crystal structure. The beam is shined through a thin layer of a sample whose crystalline structure acts as a diffraction grating. Then, the electron beam is scattered into a diffraction pattern. The result diffraction pattern can be observed on a screen or film.

### How to interpret the data



**Figure 1:** An example of an electron microscopy image of inorganic tantalum oxide.

*The circle indicates the thin region that was further analyzed.*



**Figure 2:** Electron diffraction pattern of tantalum oxide shown above.

*The brightest spot in the middle is the beam that passed through the sample without diffracting.*

The area that is usually chosen for the crystal structure analysis is the very thin area close to the edge of the sample, shown in Figure 1. The observed pattern in Figure 2 shows the interference of the diffracted electron. The images are actually very sensitive to defocus of the objective lens, bright spots could turn into dark spots on the other objective lens. The thickness of the sample also influences the contrast of the images making the analysis challenging. There are two methods to solve this problem, which are exit-wave function reconstruction method, and crystallographic image processing. The exit-wave function reconstruction requires several TEM images with different defocus for the computation of the exit-wave function, while crystallographic imaging processing only needs one image, which is suitable for the samples that could be damaged by the electron beam. Further improvement can be performed using crystal tilt compensation and searching for the most likely projected symmetry.

### Good literature examples

1. Bendersky, L. A.; Gayle, F. W. Electron Diffraction Using Transmission Electron Microscopy. *J Res Natl Inst Stand Technol.* **2001.** 106(6), 997–1012.

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[https://en.Wikipedia.org/wiki/Electron\\_crystallography](https://en.Wikipedia.org/wiki/Electron_crystallography)

[https://en.Wikipedia.org/wiki/Crystallographic\\_image\\_processing](https://en.Wikipedia.org/wiki/Crystallographic_image_processing)

<https://www.britannica.com/science/electron-diffraction>

Kohli, Rajiv. Developments in Imaging and Analysis Techniques for Micro- and Nanosize Particles and Surface Features. In *Developments in Surface Contamination and Cleaning: Detection, Characterization, and Analysis of Contaminants*; Kohli, R., Mittal, K. L., Eds.; Elsevier: Cambridge, MA, 2012; pp 215-306.

### Useful resources for in-depth reading

Samney, W. L. Understanding Transmission Electron Microscopy Diffraction Patterns Obtained From Infrared Semiconductor Materials. Adelphi, MD: Army Research Laboratory, 2013.

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## Other diffraction techniques

Student authors: Katie Kidder 2018

### How electron/neutron and SAXS/WAXS different

Electron Diffraction, a beam of electrons is shot at a thin layer of a material, on the order of 100 nm. Is the only reliable method for obtaining crystal structure information on crystals that are on the order of 0.01 nm in diameter. Single crystal electron diffraction produces Kikuchi lines which can be used to align crystals for TEM.

Example [Some indexed Kikuchi lines for a \[110\]bcc diffraction pattern when the crystal is oriented precisely along the \[110\] zone axis](#)

Neutron Diffraction, neutrons are generated by a nuclear reactor and then sent through a monochromator before being scattered through the crystal. Neutrons are scattered differently by atoms than x-rays are. For example hydrogen does not diffract x-rays well, whereas neutrons are very strongly scattered by hydrogen

SAXS, small angle x-ray scattering. WAXS, wide angle x-ray scattering. SAXS is done with an angle  $2\theta$  less than 5 degrees and is most often used to examine features greater than 50 nm in size. WAXS is done with an angle of greater than 5 degrees. WAXS is generally used to examine polymers and can be used to detect features in the approximately 10 nm or less area.

#### 2. How to interpret the data it generates

These techniques are presented similarly to XRD in that they provide verification of crystal structure. Two compounds with the same pattern have the same crystal structure. These techniques are frequently used in conjunction with other data to support that a synthesis has been successful by comparing with a reference pattern, or by indicating that a change in the pattern has occurred over the course of the synthesis

Another use of these diffraction methods is crystal structure determination. This can be done due to the fact that a peak at each wavelength or angle (for electron/neutron or x-rays) corresponds to a certain plane in the crystal structure. If there is a peak in the spot that corresponds to the miller index, then there is something in the sample in that plane that diffracted the (x-ray/electrons/neutrons). Based on these a crystal structure can be determined, most often by comparing to a structure library.

#### Caveats/Errors

1. Electron Diffraction: Secondary Diffraction (ie the electron is scattered by multiple points in the crystal lattice) can lead to extra reflections and unreliable! beam intensities.
  1. Can only be used on very small quantities of sample
2. Neutron Diffraction
  1. Incredibly Expensive, and requires one cubic millimeter of sample
  2. Beams of neutrons are weak
3. SAXS/WAXS
  1. Same problems as XRD since they still utilize x-rays (phase problem- cannot measure the electric field, only the intensity of the x-ray but the Electric field also depends on the phase).

Broad peaks implies an amorphous crystal structure.

<https://www.chem.uci.edu/~lawm/263%204.pdf>

#### 3. Good literature examples

This paper was looking at hydrogen content in an MX-ene. Since hydrogen scatters neutrons so strongly over a large range of wavelengths, it becomes part of the background. This paper looked at the difference between a sample with no hydrogen and a sample with a know combination of hydrogen, and then looked at a linear combination of the two in order to determine the amount of hydrogen in an unknown sample. Since all the other peaks match up, the presence of hydrogen is the only difference in this crystal structure.<sup>1</sup>

Figure 1

Figure 2

This paper was looking at the digestion of milk in the absence (Figure 1) and the presence (Figure 2) of bile compounds, and what nanostructures formed over the course of the digestion process. This paper used SAXS to look at the digestion over time. Two things can be interpreted from the figures. First it is clear that the crystal structure of the milk changes over the course of the digestion due to the fact that peaks both appear and disappear over time and with change in pH. Secondly it can be determined what the crystal structure at each point is by assigning the peaks to their corresponding Miller indices and then comparing which crystal structure those assignments belong to. The structures are shown alongside Figure 1. [2](#)

#### Bibliography

(1) Muckley, E. S.; Naguib, M.; Wang, H.-W.; Vlcek, L.; Osti, N. C.; Sacci, R. L.; Sang, X.; Unocic, R. R.; Xie, Y.; Tyagi, M.; Mamontov, E.; Page, K. L.; Kent, P. R. C.; Nanda, J.; Ivanov, I. N. *ACS Nano* **2017**, *11*, 11118–11126.

(2) Salentinig, S.; Phan, S.; Khan, J.; Hawley, A.; Boyd, B. J. *ACS Nano* **2013**, *7*, 10904–10911.

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## WAXS and SAXS

Student authors: Katie Kidder 2018 & Xueying Lyu 2019

### WAXS (Wide-angle X ray scattering):

In X-ray crystallography, is the analysis of Bragg peaks scattered to wide angles, which are caused by sub-nanometer sized structure. It is used to determine the crystalline structure of the polymers. The diffraction pattern can be used to determine the chemical composition or phase of the films, and the size or texture of the films. Wide-angle X-ray scattering is the same technique as Small-angle X-ray Scattering (SAXS), except that the distance from sample to the detector is shorter and thus diffraction maxima at larger angles are observed for WAXS.

#### How does the technique work?

The sample is scanned in a wide-angle X-ray goniometer. A goniometer is an instrument that either measures the angles or allows an object to be rotated to a precise angle. X-rays are scattered by the electrons in a material. The scattering intensity is plotted as a function of the  $2\theta$  angle. WAXS usually covers angular 5-60 degree. For SAXS, it covers much smaller angle, which is up to 1 degree.

When X-rays are directed at the solids, they are scattered in some certain patterns depend on the internal structure of the material. A crystalline solid can consist of regularly spaced atoms (electrons) that are referred as imaginary planes. The distance between the imaginary planes is called d-spacing. The intensity of the d-spacing is proportional to the number of electrons/atoms in the structure. Since every crystal solid as its unique pattern of d-spacing (powder pattern) , the chemical characteristics can be determined.

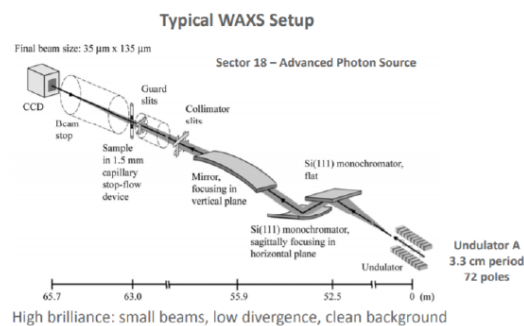


Figure 1. Wide-angle scattering set up. FR.F. Fischetti et al, The BioCAT undulator beamline 18ID: a facility for biological non-crystalline diffraction and X-ray absorption spectroscopy at the Advanced Photon Source (2004) J. Synch. Rad. 11:399 – 405.

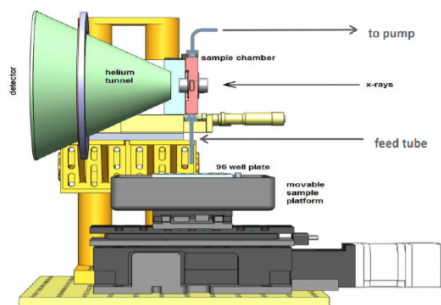


Figure 2. Portable WAXS set up with sample autolader.

#### How to interpret the data?

The position of the peak from WAXS spectra can indicate the presence of certain structure.

For example, the peaks in WAXS spectra (Figure 3 ) indicates the composition of the protein myoglobin (black) and hemoglobin (red).

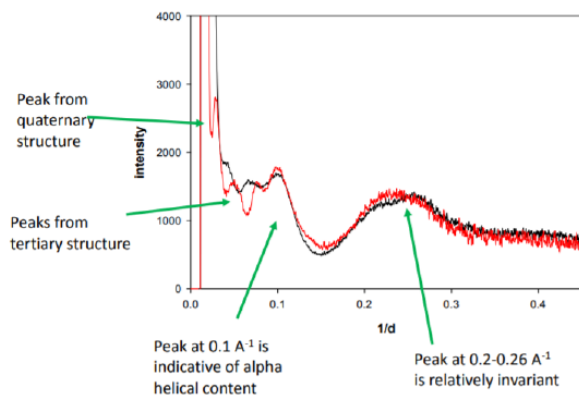


Figure 3. The WAXS spectra of myoglobin (black) and hemoglobin (red).

#### Good Literature Example:

G. A. Waychunas, C. C. Fuller, B.A. Rea, J.A. Davis, "Wide angle X-ray scattering (WAXS) study of "two-line" ferrihydrite structure: Effect of arsenate sorption and counterion variation and comparison with EXAFS results", *Geochimica et cosmochimica Acta*, **1996**, 60, 1765-1782.

#### Reference:

[https://en.Wikipedia.org/wiki/Wide-angle\\_X-ray\\_scattering](https://en.Wikipedia.org/wiki/Wide-angle_X-ray_scattering)

<https://www.malvernpanalytical.com/en/products/technology/xray-scattering>

<https://www.embl-hamburg.de/biosaxs/courses/embo2012/slides/high-brilliance-waxs-fischetti.pdf>

<https://www.diamond.ac.uk/Science/Research/Techniques/Diffraction/Scattering.html>

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## X-ray diffraction (XRD) basics and application

### How the Technique Works

X-ray diffraction is a common technique that determine a sample's composition or crystalline structure. For larger crystals such as macromolecules and inorganic compounds, it can be used to determine the structure of atoms within the sample. If the crystal size is too small, it can determine sample composition, crystallinity, and phase purity. This technique sends x-ray beams through it. X-ray beams are chosen because their wavelength is similar to the spacing between atoms in the sample, so the angle of diffraction will be affected by the spacing of the atoms in the molecule, as opposed to using much larger wavelengths, which would be unaltered by the spacing between atoms. The x-rays then pass through the sample, “bouncing” off of the atoms in the structure, and changing the direction of the beam at some different angle, theta, from the original beam. This is the angle of diffraction. Some of these diffracted beams cancel each other out, but if the beams have similar wavelengths, then constructive interference occurs. Constructive interference is when the x-ray beams that are whole number integers of the same wavelength add together to create a new beam with a higher amplitude. The greater amplitude of the wave translates into a greater signal for this specific angle of diffraction. The angle of diffraction can then be used to determine the difference between atomic planes using [Bragg's law](#),  $\sin\theta = n\lambda/2d$  where lambda is the wavelength added, theta is the angle of diffraction, and d is the distance between atomic planes. The distance between atomic plates can then be used to determine composition or crystalline structure.

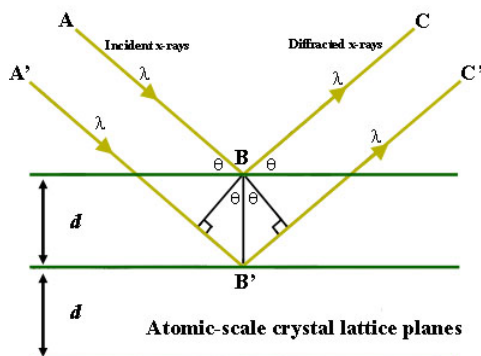


Figure 1. Bragg's Law reflection. The diffracted X-rays exhibit constructive interference when the distance between paths ABC and A'B'C' differs by an integer number of wavelengths ( $\lambda$ ). Figure Courtesy of Creative Commons license and found on [https://serc.carleton.edu/msu\\_nanotech/methods/BraggsLaw.html](https://serc.carleton.edu/msu_nanotech/methods/BraggsLaw.html)

### Useful Visualization of X-ray Diffraction

- [https://www.doitpoms.ac.uk/tlplib/xray-diffraction/bragg\\_php](https://www.doitpoms.ac.uk/tlplib/xray-diffraction/bragg_php)

### How to interpret the data

The result of X-ray diffraction plots the intensity of the signal for various angles of diffraction at their respective two theta positions. The two theta positions correspond to a certain spacing between the crystals or atoms in the samples, determined by the angle of diffraction from the incident x-ray beam sent into the sample. The intensity of the peaks is related to the amount of molecules in that phase or with that spacing. The greater the intensity of the peak, the greater the amount of crystals or molecules with that distinct spacing.

The width of the peaks is inversely proportional to the crystal size. A thinner peak corresponds to a bigger crystal. A broader peak means that there may be a smaller crystal, defect in the crystalline structure, or that the sample might be amorphous in nature, a solid lacking perfect crystallinity. For smaller samples, the patterns determined using XRD analysis can be used to determine a sample's composition. There is a large database of elements, compounds, and minerals that contain the diffraction patterns for elements, compounds, and minerals. The pattern for an unknown compound can be compared to the literature and experimentally determined values to verify the identity of an element, matching both the location, width, and relative heights of the diffraction patterns.

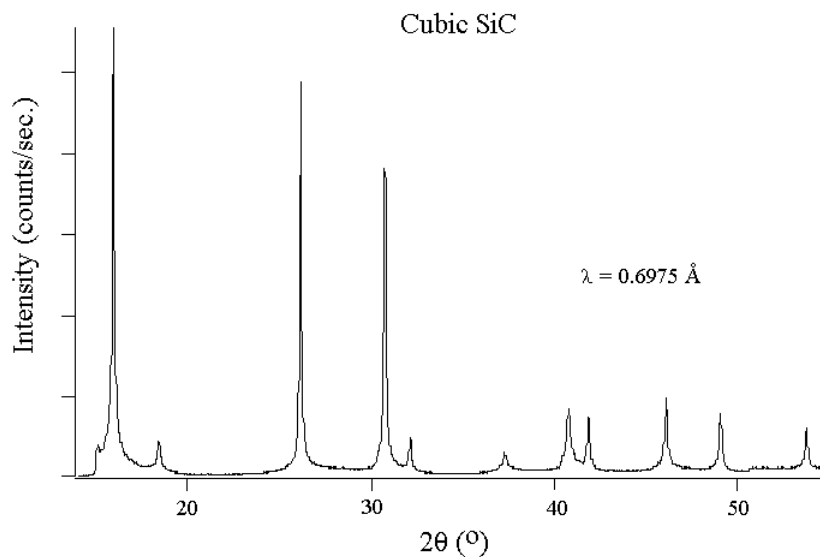


Figure "2" Figure courtesy of Creative Commons license and can be found at <https://serc.carleton.edu/details/images/20376.html>

### Good literature examples

- <https://www.ncbi.nlm.nih.gov/pubmed/25459903>
- <https://link.springer.com/article/10.1186/2228-5326-3-8>

### Works cited

1. X-ray Diffraction @ McGill <http://eps.mcgill.ca/xrd/howxrdworks.html> (accessed May 3, 2019).
2. Bragg's Law [https://serc.carleton.edu/msu\\_nanote...BraggsLaw.html](https://serc.carleton.edu/msu_nanote...BraggsLaw.html) (accessed May 3, 2019).
3. DoITPoMS - TLP Library X-ray Diffraction Techniques - Relationship between crystalline structure and X-ray data <https://www.doitpoms.ac.uk/tlplib/xr...ction/peak.php> (accessed May 3, 2019).
4. Diffraction Basics | Chemical Instrumentation Facility | Iowa State University <https://www.cif.iastate.edu/acide/xrd-tutorial/xrd> (accessed May 3, 2019)

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## CHAPTER OVERVIEW

### Electrochemistry

[Cyclic Voltammetry \(CV\)](#)

[Impedance Spectroscopy](#)

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## Cyclic Voltammetry (CV)

Student authors: Zichen Zheng 2018 & Zhengzhou Qiu 2019

### How CV works

Cyclic voltammetry (CV) is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation processes of molecular species. Figure 1.1 shows an example of cyclic voltammetry.

Figure 1. An example of cyclic voltammetry.

### 3. How do we set up the experimental instruments to get CV data?

**Reference Electrode (RE)** has a well-defined and stable equilibrium potential. It is used as a reference point against which the potential of other electrodes can be measured in an electrochemical cell (Figure. 2)

Figure 2. A brief picture of Cu-Cu(II) reference electrode.

**Working Electrode (WE)** carries out the electrochemical event of interest.

### 4. Steps of collecting the data (optional)

1. Recording background scan.
2. Measure the open circuit potential (OCP). When the electrochemical cell is assembled, and the analyte has been added, a potential develops at the electrodes. The potential can be observed when no current is flowing is called OCP. OCP gives information about the redox state of the materials in solution as well as the concentration of different species when the solution contains a mixture.<sup>1</sup>
3. RE and WE create undesired resistance, i.e. ohmic drop. So we need to minimize it.
4. Recording the cyclic voltammogram. The electrodes are connected to the potentiostat, and the experimental parameter will be set up through the potentiostat software.

### How to interpret the data

- Clear up the confusion: there are two ways of making the CV graph, one is US Convention and the other is IUPAC Convention.

Basic elements of the CV profile

- X-axis: the applied potential (E) that is imposed to the system
- Y-axis: the resulting current (i) that is passed.
- The arrow indicates the beginning and sweeps direction of the first segment (or “forward scan”)
- In the caption of Figure 1, there was a value of “ $v = 100 \text{ mV/s}$ .”  $v$  is the scan rate. It means that during the experiment the potential was varied linearly at the speed (scan rate) of 100 mV per second.
- From A to D, the potential is scanned negatively (cathodically); it switches at point D, and from D to G the potential is scanned positively (anodically). So the full cycle goes as A  $\rightarrow$  D  $\rightarrow$  G.
- From A to D, the  $[\text{Fc}^+]$  is reduced to Fc. At point C, the peak cathodic current ( $i_{p,c}$ ) is observed. The current indicates the diffusion of  $\text{Fc}^+$  from the surface of electrode.
- The volume of solution at the surface of the electrode containing the reduced Fc, called the diffusion layer, continues to grow through the scan. So  $\text{Fc}^+$  transport to the electrode slower. So as scanning to more negative potentials, the rate of diffusion of  $\text{Fc}^+$  from the bulk solution to the electrode surface becomes slower, resulting in a decreased current.
- At point D, the scan direction reversed. As the  $[\text{Fc}^+]$  decrease and  $[\text{Fc}]$  increase, Fc is oxidized back to  $\text{Fc}^+$ .
- At B and E,  $[\text{Fc}^+] = [\text{Fc}]$
- At C and F, we have the estimated  $E^0$
- **some CV figures with abnormal shapes.**
  - When there are multiple peaks, it means that there are probably multifold redox reaction happening
  - The curves are not smooth: depends on how the molecules in the electrolyte move to/out of the electrode’s surface to do the reaction/after finished reacting with the electrodes. Since the electrolyte is not stirred, there might be some delay in the molecule’s motion
- Another ~potential~ CV graph
- This is not as “duck-shaped” as the other examples

- This is of potential electrode material, so once a certain potential is applied to the system it jumps up to a near-maximum current (current comes from the electrolytes adsorbing to the electrode surface, so reaching a high current quickly means there are high charge/discharge rates). When the scan is reversed it drops back down to a near minimum current. For supercapacitor electrodes that depend on fast charge/discharge rates a more rectangular graph is ideal
- This also shows cyclability, so having a similar shape at high scan rates (blue vs orange) means that it has high cyclability

### Importance of the scan rate

- It controls how fast the applied potential is scanned.
- Faster scan rate → smaller diffusion layer → more electrons coming → higher currents

### Works cited

1. Elgrishi, N; Rountree, K. J; McCarthy, B. D.; Rountree, E. S; Eisenhart, T. T; Dempsey, J. L. *Journal of Chemical Education* **2018** 95 (2), 197-206
- 2.

### Further reading and practice

1. The [supporting information](#) of Dempsey's paper<sup>1</sup> is a good source for practicing.
2. You can also visualize the scan in CV cycle on [this website](#).

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## Impedance Spectroscopy

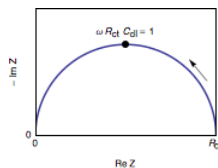
Student authors: Han Le 2019

### How impedance spectroscopy works

**Impedance** ( $Z$ ) is quite similar to resistance: it is a measure of the ability of a circuit to resist current. Resistance is a concept for ideal resistors, but many circuits are more complex (they do not exactly follow Ohm's Law, independent of frequency, no phase shift between current and voltage signals), so impedance is used to replace resistance instead. Impedance takes into account all the considerations limited to an ideal resistor and other factors such as inductance, resistance, and capacitance. During electrochemical impedance spectroscopy (EIS), an AC voltage is applied to a sample at different frequencies and the electrical current is measured. Impedance ( $Z$ ) can then be calculated as the ratio of the frequency-dependent potential ( $E$ ) to the frequency-dependent current ( $I$ ). This technique allows for multiple frequency measurements. It can be used to probe different electrochemical processes happening at the same time, electron transfer rate of reaction, diffusion-limited reactions, or capacitive behavior of a system. Some of the applications of EIS includes detecting corrosion of metals, characterizing aging of food, measuring bacterial concentration in label-free biosensors, and studying ion mobility in batteries and supercapacitors.

### How to interpret the data

Since impedance can be expressed as a complex number, it can be plotted as a Nyquist plot (the real part on the x-axis, and the imaginary part on the y-axis). Most of the times this plot is a semicircle, which signifies a charge transfer process, and the size of the semicircle represents how much charge transfer resistance we have. However, this plot can also look like a straight line with positive slope if it is a diffusion process (called Warburg impedance). This plot is also dependent on the circuit (parallel, series, or combinations). Apart from Nyquist plots, impedance can also be presented as a Bode plot.



**Figure 1:** Nyquist plot of a RC parallel circuit. The arrow indicates increasing angular frequencies. Image author: Enseeg (Wikipedia), used under Creative Commons Attribution-Share Alike 4.0 International license.

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## CHAPTER OVERVIEW

### Electron and Probe Microscopy

Atomic Force Microscopy (AFM)

Basic TEM

Scanning electron microscopy (SEM)

TEM: Bright field versus dark field

Transmission electron microscopy (TEM): TEM versus STEM and HAADF

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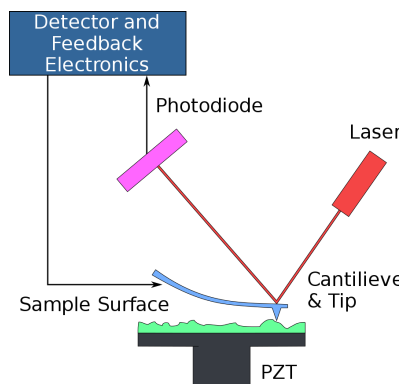
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## Atomic Force Microscopy (AFM)

Student authors: Trexler Hirn 2018 & Boxi Li 2019

### How AFM works

Atomic force microscopy works by the sample being moved in an X,Y grid beneath a sharp tip attached to the free end of a cantilever being passed along the surface of the material in question. This process is demonstrated in figure 1 below. The cantilever reflects a laser to a photodiode. The contact with the tip to the material can be an atomic scale phenomenon signal from, but the motion of the cantilever is a macro scale movement. This movement is measured by the reflected movement of a laser on the photodiode which is converted to an electrical signal giving information on the measurements. (sometimes there are different ways of measuring the cantilever movement including a direct deflection on an oscillator that converts a change from equilibrium into an electrical signal.)



**Figure 1. Scheme of AFD mechanism.** <sup>2</sup>

For imaging purposes AFM can be used in contact mode (where the tip drags along the surface of the material) tapping mode (where the cantilever oscillates at a specific frequency and the surface disrupts the regularity of the oscillation) and non-contact mode (cantilever oscillates just above the surface of the material and van der waals forces disrupt the oscillation)

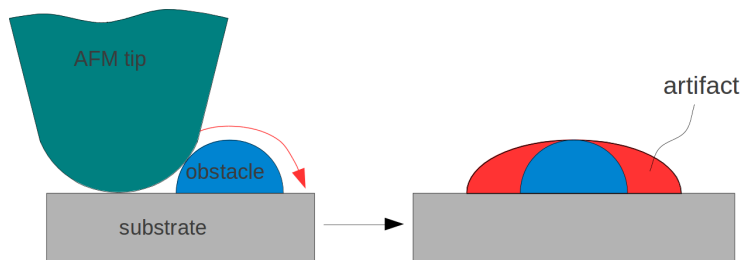
AFM can also be used for force spectroscopy when the cantilever is extended towards the material and the disruption to the cantilever is disrupted giving information on nanoscale forces such as atomic bonding and van der waals forces.

### How to interpret the data

For imaging purposes, the data is usually presented as a topographical “heat map” with a colored scale to show height/depth and a scale for the X,Y plane to show measurements between peaks/valleys etc. Interpreting the data specifically depends on the type of imaging and the material being imaged, but the general output shows the topography with information on smoothness as well as “hardness” due to differing forces experienced by the tip during the scan.

For force microscopy, force curve readouts are available to correspond with loci on the sample giving the ability to correlate the forces with topography.

ERROR: A common source of error to consider is the shape and sharpness of the tip with regard to the surface morphology (as shown in Figure 2 below). If the radius of the tip is too large the refinement of the measurement may be smoothed. Similarly, due to the nature of the tip, AFM cannot measure steep walls/overhangs.



**Figure 2. Showing an AFM artefact arising from a tip with a high radius of curvature with respect to the feature which is to be visualized**<sup>3</sup>

Also the slow scanning time can lead to thermal drift making measurements between topographical features less accurate.

### Good literature examples

Figure 3 is from a paper<sup>1</sup> that was investigating an organic-inorganic composite of phosphomolybdic acid (PMA) and PEDOT:PSS electron transport layer that is printed on top of the photoactive layer of a semi transparent organic solar cell.

Their use of AFM was to compare the previous technique (just PMA) to their hybrid of PMA:PEDOT:PSS. Figure 2a shows the surface morphology of the photoactive layer which they report is very smooth with a root mean squared roughness of 1.3 nm. Figure 2b shows AFM of just PMA deposited on the photoactive layer and indicates a much rougher surface with a RMS roughness of 4.2 nm, in addition to large isolated islands and non-uniform distribution of PMA. Figure 2c shows AFM of PMA:PEDOT:PSS deposited on the photoactive layer and reveals a fairly smooth and uniform surface. The RMS roughness is slightly greater than the photoactive layer at 1.9 nm, but there are no aggregations and rough islands like just the PMA. This AFM supports the notion that the smoother surface achieved with PMA:PEDOT:PSS will have a good interface contact between the organic photoactive layer and anode.

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## Basic TEM

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### How TEM works

#### How to interpret the data

The electron beam in TEM can be deflected, leading to variation in contrast, for to several reasons. These different reasons are called different "contrast mechanisms" and affect how you interpret TEM data.

#### Mass-thickness contrast

x

#### Z-contrast

x

#### Diffraction contrast

x

### Good literature examples

#### Mass-thickness contrast

x

#### Z-contrast

x

#### Diffraction contrast

x

### Works cited

### Useful resources for in-depth reading

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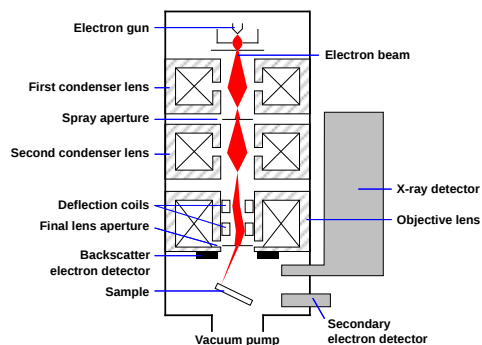


## Scanning electron microscopy (SEM)

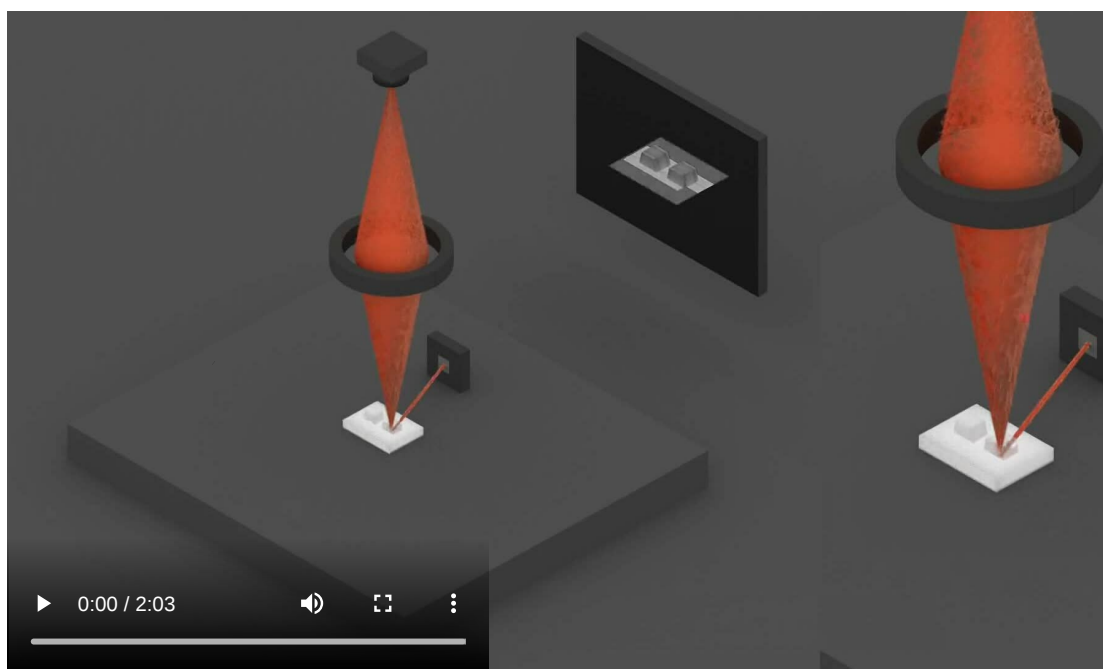
Student author: Emily Nagle 2019

### How SEM works

In an SEM, an electron beam is emitted from an electron gun, then narrowed to a size of approximately 0.4-5 nm in diameter through the use of one or two condenser lenses. The beam then passes through a pair of deflection coils in the electron column to deflect the beam in the x and y axes before interacting with the sample. This deflection ensures that the scan is in a raster fashion, which means it is a rectangular image capture pattern of the sample. When the electron beam interacts with the sample, it loses energy due to random scattering and absorption by the sample. A schematic showing the components of SEM and how it works is shown in Figure 1. Additionally, a video explaining how SEM works is provided.

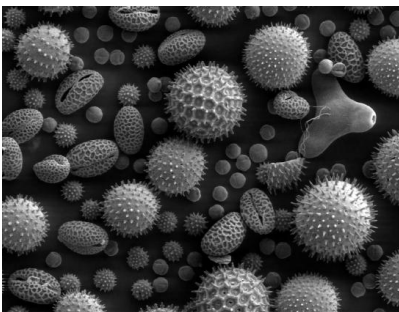


**Figure 1:** Schematic of how an SEM works (Figure courtesy of Creative Commons license and can be found at [https://en.Wikipedia.org/wiki/File:Schema\\_MEB\\_\(en\).svg](https://en.Wikipedia.org/wiki/File:Schema_MEB_(en).svg))



**Video 1:** Illustration of how SEM works courtesy of Creative Commons license and found at [https://en.Wikipedia.org/wiki/File:Scanning\\_Electron\\_Microscope.ogv#filehistory](https://en.Wikipedia.org/wiki/File:Scanning_Electron_Microscope.ogv#filehistory)

The electron beam of a scanning electron microscope interacts with atoms at different depths within the sample to produce different signals including secondary electrons, back-scattered electrons, and characteristic X-rays. Each of these signals has its own detector in the SEM, as seen in Figure 1. Secondary electrons are low energy electrons that are ejected from the valence or conduction bands of atoms in the sample through inelastic scattering from the beam electrons. Back-scattered electrons are electrons from the beam that are reflected through elastic scattering interactions with atoms in the sample. The intensity of the back-scattered electron signal is dependent upon the atomic number so it can provide information about the distribution of different elements in a sample. The characteristic X-rays are emitted when the electron beam interacts with the sample and removes an inner shell electron, resulting in a higher-energy electron filling the shell and releasing energy. The energy or wavelength of these X-rays can be measured by Energy-dispersive X-Ray Spectroscopy to identify and measure the abundance and distribution of elements in the sample. The electron beam absorbed by the sample is detected and used to create an image of the sample distribution. The resulting image is a map displaying the intensity of signal emitted from the area of the sample being scanned, as seen in Figure 2. Additionally, EDS detectors can be attached to the SEM for elemental analysis.



**Figure 2:** SEM image of pollen grains. Image released to the public domain by original author Dartmouth College Electron Microscope Facility and found at [https://upload.wikimedia.org/Wikipedia/commons/a/a4/Misc\\_pollen.jpg](https://upload.wikimedia.org/Wikipedia/commons/a/a4/Misc_pollen.jpg)

In order to obtain SEM images, the sample must be electrically conductive at the surface as well as electrically grounded so that it does not accumulate charge. Samples are mounted onto the specimen holder using a conductive adhesive. Metal samples require minimal sample preparation other than conductively mounting the sample to the stage. Non-conductive materials typically undergo ultrathin coating with electrically conductive materials such as gold, platinum, chromium, or graphite. The coating is accomplished through sputter-coating or evaporation under high vacuum.

### How to Interpret the Data

Different SEM images can be produced based on the type of detector being used and these image can be used to see what the sample looks like on the nanoscale. The most typical detector used detects the secondary electrons that are emitted from the sample by inelastic scattering. The number of secondary electrons detected represents the signal intensity and is combined with the position of the beam to produce a gray-scale images showing the sample's topography, as seen in Figure 2. Back-scattered electrons can also be used to get an image since elements will reflect a different number of electrons. Therefore, the intensity of back-scattered electrons will vary throughout a sample depending on the elements present. An SEM image produced from the intensity of back-scattered electrons and the beam position can show the distribution of different elements in the sample. Elements that are heavier and reflect more electrons will appear brighter in the image so back-scattered electrons can show contrasts in chemical composition. However, the identity of the different elements cannot be determined with SEM alone, an EDS attachment would have to be used to quantify the relative abundance of different elements.

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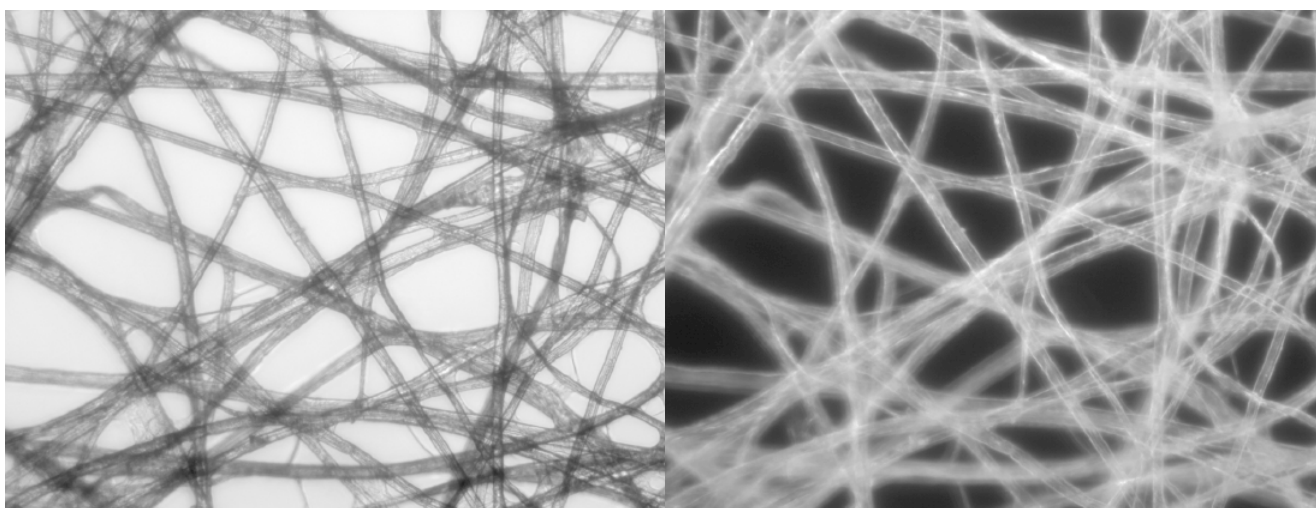
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## TEM: Bright field versus dark field

Student authors: Bobby Gaston 2018 & Han Le 2019

### How bright field and dark field TEM are different

One of the main differences between the bright field and dark field mode is which electron populations are used to construct the TEM image. Bright field image is the most common image generated with a TEM. Some areas of the sample can absorb or scatter electrons and appear darker, while other areas that transmit electrons appear brighter. In the bright field image the unscattered (transmitted) electron beam is selected with the aperture, and the scattered electrons are blocked. Since the unscattered beam is selected, areas with crystalline or high mass materials will appear dark. On the other hand, in dark field mode, the unscattered electron beam is excluded from the aperture, and the scattered electrons are selected instead. Hence, the areas where there are no electron scattering and (e.g. the areas around the sample) will be black, while the areas with materials will appear bright. This technique can be used to enhance contrast when the bright field image is not clear enough, especially when imaging crystalline features that are too small or are drowned out of view. It can also be used to study the crystal lattice, crystal defects, stacking faults, dislocations and particle/grain size.



**Figure TEM. 1 :** TEM image of a tissue paper sample in bright field mode (left) and dark field mode (right). Image author: Zephyris (Richard Wheeler, Wikipedia), used [under Creative Commons Attribution-Share Alike 4.0 International license](#).

### How to interpret the data

TEM dark field and light field image can be used to characterize the size and morphology of the sample as well as their crystal lattice. The most common sources of image contrast are particle mass and crystallinity. Heavier atoms scatter electrons more intensely than lighter atoms. Hence, in bright field mode, the regions with heavier atoms are darker, while in dark field mode these regions are brighter. In biological and polymeric samples with low atomic number, staining can help enhance the image contrast. Samples that are more crystalline are also more strongly diffracted and will appear darker in bright field mode, and brighter in dark field mode. The most common sources of error associated with TEM images are associated with aligning and positioning a sample. It is also important to note that the smaller the aperture size, the higher the contrast will be.

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## Transmission electron microscopy (TEM): TEM versus STEM and HAADF

Student authors: Melissa Bollmeyer 2018 & Boxi Li 2019

### How TEM, STEM, and HAADF are different

While light microscopes use visible light (400-700 nm), electron microscopes use beams of electrons, which have wavelengths about 10,000 times shorter.<sup>1</sup> The shorter wavelengths allow for the images to be better resolved, down to about 0.1 nm. An electron beam is produced by heating a tungsten filament and is focused using magnetic fields.<sup>2</sup> A high vacuum is needed to prevent collisions between the high-energy electrons and air molecules, which would absorb energy from the electrons.

To obtain a TEM image, a thin sample of about 200 nm is subjected with a high energy electron beam., which is directed using electromagnetic lenses. The electrons are elastically or inelastically scattered as they penetrate the sample. Either the transmitted electrons or the scattered electrons can be imaged, known as dark-field and light-field imaging, respectively (See Bright/Light field versus dark field and EDS). Although atomic resolution is theoretically possible, it is difficult to achieve due to defects in the lenses.

Imaging depends on contrast, which can arise from three processes: mass-thickness contrast, diffraction contrast, and phase contrast.<sup>3</sup>

1. Mass-density contrast: Scattering increased with the atomic number and thickness of the sample. For example, contrast in amorphous materials arises from mass-density contrast. This is often the case for biological materials.
2. Diffraction contrast: Electrons are deflected according to Bragg's law and depends on the crystal structure. Often this is used to examine crystal lattice defects.
3. Phase contrast: Several beams are admitted on the sample, and the interaction of the deflected beams with the transmitted beams give high-resolution images useful for determining crystal structure.

### STEM (Scanning transmission electron microscopy)

STEM is similar to TEM. While in TEM parallel electron beams are focused perpendicular to the sample plane, in STEM the beam is focused at a large angle and is converged into a focal point. The transmitted signal is collected as a function of the beam location as it is rastered across the sample.

There are multiple detectors for STEM imaging:

1. BF (bright-field) detector: small angles (<0-10 mrad). These images are similar to the bright-field images obtained using TEM.
2. ADF (annular dark-field) detector: larger angles (10-50 mrad)
3. HAADF (high-angle annular dark-field) detector: Angles > 50mrad

None of the elastically scattered electrons reach the detector, so it only images from inelastically scattered electrons. This is also known as Z-contrast imaging because there is a direct correlation between the local contrast and local mass-thickness, which depends on the atomic number Z. HAADF imaging allows for enhanced contrast, especially at lower atomic numbers, compared to TEM.

### How to interpret the data

Characteristics of solids such as structure, morphology, and crystallite size can be studied using electron microscopes, often to characterize defects and elemental distribution.<sup>2</sup> STEM is particularly useful for examining particle size, crystal morphology, magnetic domains, and surface defects. TEM is useful for imaging the bulk structure, allowing better observations of crystal defects.

Contrast in the image is produced by the scattering of electrons due to their interaction with atoms in the sample. Scattering depends on thickness of the sample as well as the material itself, where heavier atoms deflect more electrons. Bright and dark areas refer to the density of electrons hitting the detector. Therefore, brighter areas correspond to where more electrons are transmitted, while darker areas correspond to where electrons are scattered. The darker the area, the heavier the atom at that location.

Possible issues that may arise are particle agglomeration and impurities.

1. Particle Size<sup>4</sup>

The size of particles can be manually determined from a TEM or STEM image by measuring the distance across the particle. To obtain an accurate particle size, the average of many particles should be used. As the particle size decreases to only several nanometers, there may be difficulties in having poor contrast between the particle and the background.

-HAADF may allow for better contrast in materials with lower Z compared to conventional TEM imaging. For an example, see Figure 1 below. Figure a shows the HAADF image of Pt nanoparticles while figure b shows the bright-field image of the same sample.

## 2. Morphology

Determining crystal morphology with TEM or STEM may be more difficult because a 2D image is produced, while morphology is a 3D property. To accurately determine the crystal morphology, the sample should be imaged along several different crystal planes. Some morphologies that might be identified are lamellar (nanosheet, plate or belt-like), nanoneedle, nanorod or nanowire. The figure 2 below [5] highlights the difficulty in determining a 3D structure with TEM. A cubic morphology may show a square 2D image if the beam is directed directly at one of the faces, but could also show a rectangular image if the cube is tilted.

Crystal habit - the external shape of a crystal. This may be easier to distinguish simply by examining the TEM or STEM image. For example, in Figure 3 below the crystal habit is cubic [6]. Other crystal habits may be hexagonal, rhombohedral, etc.

## 3. Crystal defects

Crystal defects may be observed in TEM or STEM images because they change the contrast in the image compared to what would be expected in a repeating crystal structure. See figure 4 below for example.

## 4. Other examples:

A. The phase boundary between between fcc silicon (Si) and hexagonal palladium silicide ( $\text{Pd}_2\text{Si}$ ) can be seen in figure 5 below. <sup>10</sup>

B. Crystal identity can be determine from the different d-spacings. In figure 6,  $\text{SnO}_2$  could be distinguished from Pt. <sup>8</sup>

## Good literature examples

One study used TEM and STEM to show the transformation of Pt-MnO heterodimers into seven different Pt-Mn<sub>x</sub> heterodimer derivatives. <sup>9</sup> Figure 7a shows the TEM and STEM-EDS images of the starting Pt-MnO material, and figure 7b shows that of Pt-MnS. It is clear that the particles maintain their morphology after the anion exchange of S for O. The anion can be distinguished by the darker contrast compared to the MnO or MnX. In the STEM-EDS image, red represent Pt, blue represents Mn, and yellow represent S. In figure 7b, the HAADF image is also shown, which has better contrast than the TEM image. Because this is a dark-field image, the Pt now appears brighter than MnS.

**Figure 7. a) The TEM and STEM-EDS images of Pt-MnO. b) The TEM, STEM-EDS, HAADF and SAED images of Pt-MnS. <sup>8</sup>**

TEM was also used to show that these particles maintained their domain size throughout the exchange process. In figure 8, the transformation of Pt-MnO to PtMnS and finally Pt-Cu<sub>2</sub>S is shown for domain sizes of Pt-MnO of a) 8 nm, b) 13 nm, and c) 23 nm. Because the scale is the same for images, it is easy to see that the domain sizes increase for a, b, and c. Moreover, it can be seen that after the ion exchange processes, the domain size is maintained.

What the TEM and STEM showed is described in figure 9 below.

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## CHAPTER OVERVIEW

### Spectroscopy

[Energy-Dispersive X-ray Spectroscopy \(EDS\)](#)

[Light absorption and photoluminescence \(PL\) spectroscopy](#)

[Raman Spectroscopy](#)

[Solid-state nuclear magnetic resonance spectroscopy \(Solid-state NMR\)](#)

[X-ray Photoelectron Spectroscopy \(XPS\)](#)

Interested in NMR, IR, or UV-vis absorption spectroscopy? [The Inorganic Spectroscopy Tutorial from the University of Alberta](#) is an excellent resource.

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## Energy-Dispersive X-ray Spectroscopy (EDS)

Student authors: Bobby Gaston 2018 & Connor Protter 2019

### What is EDS?

Energy-dispersive X-ray spectroscopy (also known as EDS, EDX, or EDXA) is a powerful technique that enables the user to analyze the elemental composition of a desired sample. The major operating principle that allows EDS to function is the capacity of high energy electromagnetic radiation (X-rays) to eject 'core' electrons (electrons that are not in the outermost shell) from an atom. This principle is known as Moseley's Law, which determined that there was a direct correlation between the frequency of light released and the atomic number of the atom.

Removing these electrons from the system will leave behind a hole that a higher energy electron can fill in, and it will release energy as it relaxes. The energy released during this relaxation process is unique to each element on the periodic table, and as such bombarding a sample with X-rays can be used to identify what elements are present, as well as what proportion they are present in.

Shown below is an example of how EDS works. The letters K, L, and M refer to the  $n$  value that electrons in that shell have (K electrons, closest to the nucleus, are  $n=1$  electrons), while  $\alpha$  and  $\beta$  indicate the size of the transition. The relaxation from M to L or L to K are therefore described as  $L\alpha$  or  $K\alpha$ , while going from M to K would be a  $K\beta$  transition. The means that are used for describing these processes as a whole are known as Siegbahn notation.

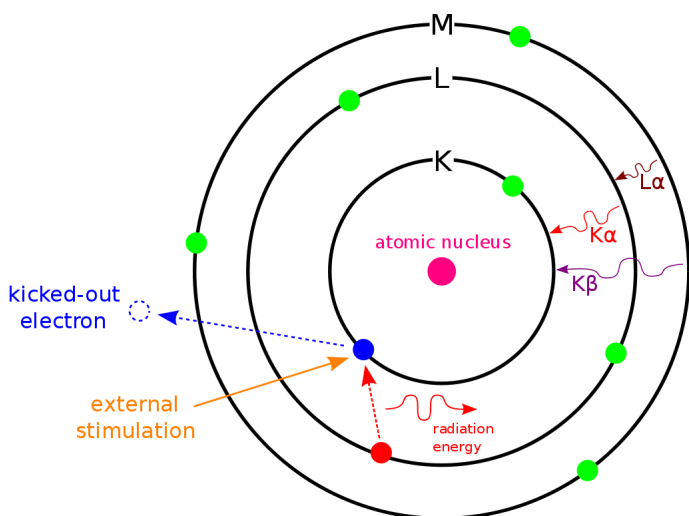
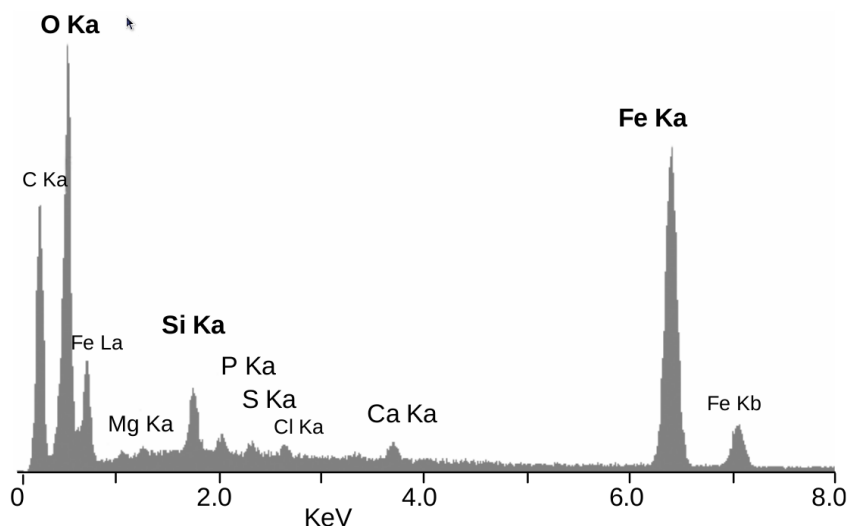


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### How is data collected?

EDS functions with a series of three major parts: an emitter, a collector, and an analyzer. These parts are additionally typically equipped on an electron microscope such as SEM or TEM. The combination of these three pieces enables analysis of both how many X-rays are released, as well as what their energy is (in comparison to the energy of the initial X-rays that were emitted).

The EDS data is presented as a graph with KeV on the x-axis and peak intensity on the y-axis. The peak location on the x-axis are converted into the atoms that the energy changes represent by a computer program.



File:EDS\_-\_Rimicaris\_exoculata.png

**Figure.** EDS chart from a research group that was analyzing the composition of shrimp and the associated bacteria that associate with these minerals. The EDS helped support the researcher's case that the endosymbiotic bacteria living on these shrimp actually do influence the iron oxide composition in these minerals. This is evident by the peaks at 0.5 and 6.5 KeV.<sup>2</sup> [Copyright of Cobari et. al and used under the Creative Commons Attribution 3.0 License.](#)

### What are some drawbacks of EDS?

Although EDS is an extremely useful technique, there are a number of difficulties involved with the process which hinder its utility. First, EDS is generally not a particularly sensitive technique. If the concentration of an element in the sample is too low, the amount of energy given off by X-rays after hitting the sample will be insufficient to adequately measure its proportion. Second, EDS generally does not work for elements with a low atomic number. Hydrogen and helium both only have an  $n=1$  shell, meaning there aren't core electrons to be removed that can allow for X-ray emission. Lithium and beryllium, meanwhile, have sufficiently low atomic numbers that the energy of X-rays given off by Li or Be samples is insufficient for measurement, and often times they cannot be tested as a result.

One additional difficulty associated with the technique is the thickness of the sample. Sample thickness can bring energy levels closer together, thus making electrons easier to move to outer energy levels, which can in turn cause deviation in the results. Another error source is overlapping emitted x-rays, which can alter the KeV readings. Additionally, X-rays are not particularly effective at penetrating beyond several nanometers in samples, which means that only surface layers can be efficiently measured by the technique. As such, if there is a discrepancy between the outer and inner material layers, it will not necessarily appear in EDS.

### Work Cited

1. [https://en.Wikipedia.org/wiki/Energy-dispersive\\_X-ray\\_spectroscopy](https://en.Wikipedia.org/wiki/Energy-dispersive_X-ray_spectroscopy)
2. <https://cfamm.ucr.edu/documents/eds-intro.pdf>
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4. L. Corbari, M.-A. Cambon-Bonavita, G. J. Long, F. Grandjean, M. Zbinden, F. Gaill, and P. Compere "Iron oxide deposits associated with the ectosymbiotic bacteria in the hydrothermal vent shrimp *Rimicaris exoculata*" *Biogeosciences* **2008**, 5, 1295–1310.

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## Light absorption and photoluminescence (PL) spectroscopy

Student author: Yuguo (Hugo) Zhang 2018 & Hang Li 2019

### How photoluminescence spectroscopy works

Photoluminescence (PL) spectroscopy is a form of light emission spectroscopy in which the light emission comes from a process called photo-excitation. As the light is directed onto a sample, the electrons within the material move into excited states. (excitation) When the electrons come down from the excited states to their equilibrium states, the energy can be released in the form of light. (relaxation) The photo-excitation and relaxation processes can be represented graphically in a figure below. (Figure 1)

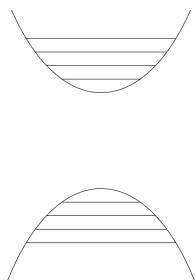


Figure 1. Schematic for excitation and relaxation processes of photoluminescence

(taken from Wikipedia on “Photoluminescence”)

Similar to fluorescence spectroscopy, a fixed wavelength is used to excite electrons and different wavelengths of light will be emitted. The intensity of the light is plotted against the wavelength on the spectrum. PL spectroscopy is useful in determining the electronic structure and properties of materials as it gives the peak light intensity that materials are able to emit for a certain wavelength.

### How to interpret the data

Interpretation of photoluminescence spectrums is relatively simple. The absorbance spectrum is created by exciting electrons at varying wavelengths while monitoring the emission at a fixed wavelength. (blue line in Figure 2) The results from a absorbance spectrum is valuable in determining the fixed excitation wavelength for the emission spectrum.

Naturally it follows that the emission spectrum is created by exciting electrons at a fixed wavelength but observing emissions at different wavelengths. (red line in Figure 2) The data extracted from an emission spectrum is often the peak emission intensity of the material, which is used to compare electronic properties.

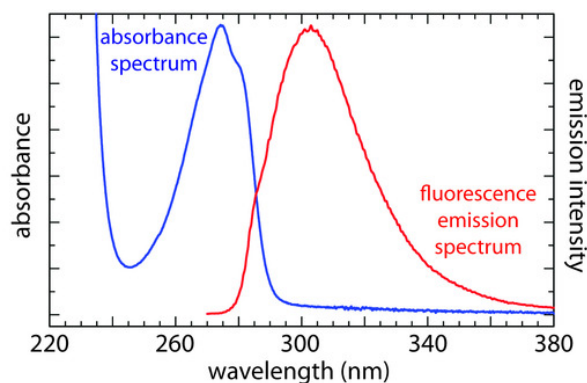


Figure 2. A sample absorbance and emission spectrum (taken from [Chemistry LibreTexts on “Photoluminescence Spectroscopy”](#))

### Transient PL

Transient Photoluminescence, also called Time-resolved Photoluminescence, is used to detect the radioactive decay of the samples in which excited electrons have a radio active decay channel. A laser beam with duration less than 10 ns is shot at the sample, and

the light emitted by the sample will decay with time. The emission is resolved and detected every several fs in a range of several ns or ms. Then the radioactive decay pattern of the excitement state is recorded.

How to interpret data:

The spectrum have intensity as y-axis and time as x-axis. The speed of excited state decay can be calculated with the intensity of light.

Good image with copyright: [Time Resolved Photoluminescence Spectroscopy \(TRPL\) by Max-Planck Institute of Polymer Research.](#)

## Good literature examples

Paper:

A. A. Mamum, T. T. Ava, K. Zhang, H. Baumgart, G. Namkoong, "New PCBM/carbon based electron transport layer for perovskite solar cells", *Phys. Chem. Chem. Phys.*, **2017**, 19, 17960-17966.

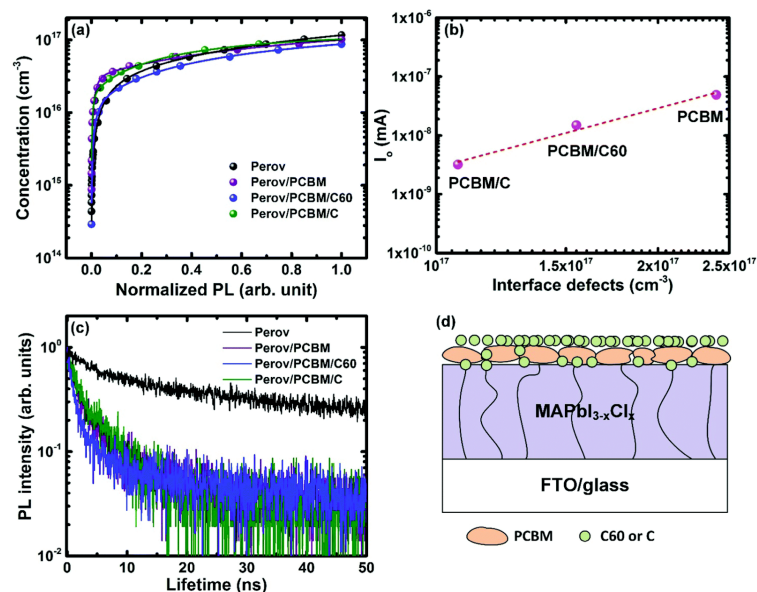


Figure 3. (a) Photogenerated carriers with PL intensity. (b) Reverse saturation current vs. interfacial defect densities. (c) Lifetime decays of different perovskite films. (d) Plausible schematic of diffusion process on the PCBM layer.

Figure 3(a) shows the concentration vs. normalized PL intensity for different materials of ETL on perovskite solar cells. Normalized PL intensity is calculated by taking the max PL intensity as "one" and normalize the rest of the data as the ratio to the max PL intensity. For each PL intensity data entry, an emission spectra was done and the peak intensity was recorded. Overall, the graph shows how different ETL materials in different concentrations emit light, and it is often used as a parameter for measuring how effective the material is as the electron transport layer.

Figure 3(c) shows the radioactive decay of the excited state. The photoluminescence intensity is decreasing over 50 ns.

## Raman Spectroscopy

Student authors: Angus Unruh 2018 & Kate Meyers 2019

### How Raman spectroscopy works

Raman Spectroscopy is performed by shining a light on a sample and measuring the intensity and wavenumber the scattered light. Most of the scattered light will be of the same intensity as the incident beam, but a small percentage will be different due to excited electrons that do not relax back to their original energy state.

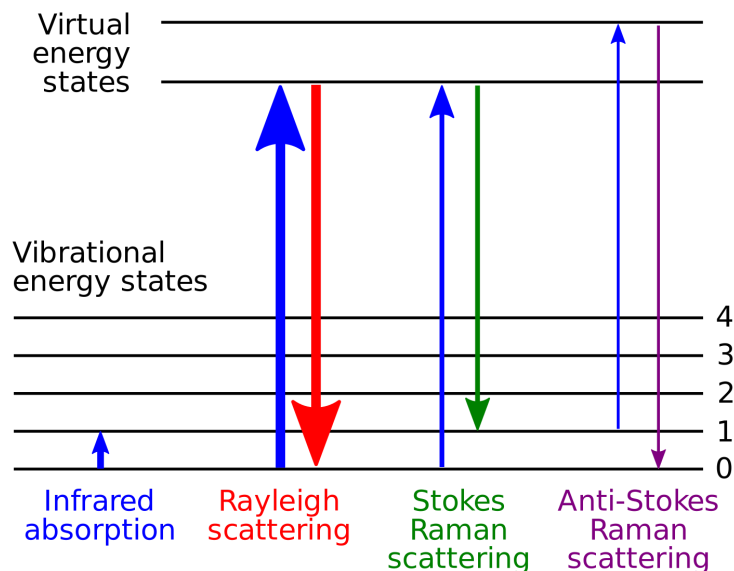


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Instead of relaxing back down to the ground state, electrons can relax to different energy levels caused by the vibrational modes of the molecules. This is similar to IR spectroscopy. By measuring the difference in initial photon and emitted photon the exact energy level of the vibrational mode can be determined.

### Advantages

- Low/no sample prep
- Raman does not alter or damage sample in any way
- Water produces very little signal (can do Raman on aqueous solutions)
- Larger range: Good for both inorganic and organic compounds
- Raman typically produces sharper peaks with less noise
- spectra are highly specific to different materials

### Disadvantages

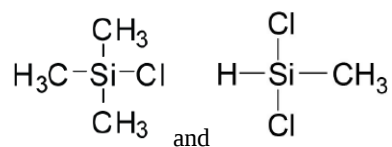
- Not appropriate for fluorescent materials
- Highly sensitive (and expensive) instrumentation required for analysis
- Can't be used for alloys or metals

### How to read the spectra

Once the energy/frequency of the vibrational modes is recorded, they can be graphed compared to intensity.

#### Example 1: $\text{Me}_3\text{SiCl}$ and $\text{MeHSiCl}_2$

Here is a Raman of  $\text{Me}_3\text{SiCl}$  and  $\text{MeHSiCl}_2$



- Each of the peaks represents a specific vibrational mode of the molecule
  - The spectra are unique to each molecule/compound. A fingerprint.
- But, as seen above, similar compounds will have some vibrational modes in common so they will likely share some similar peaks.
- The intensity of the peaks is directly proportional to the number of molecules that create the band.
  - This allows for one to quantitatively measure the concentration of molecules.

Basically, Raman can be read like an IR, where characteristic peaks/bands are identified and used to qualitatively characterize the components of a molecule.

### Example 2:

It is especially useful for characterizing inorganic compounds, aqueous solutions, or samples that you do not want to damage. A notable example of a sample that can only be reasonably be characterized with Raman is oil paintings

“Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection”

<https://www.sciencedirect.com/science/article/pii/S138614250800646X>

<https://doi.org/10.1016/j.saa.2008.11.029>

Most oil paints, such as those used in the renaissance era, were made by combining organic oil with ground up inorganic and organic pigments

- If an important painting, such as the Mona Lisa were to be restored the exact pigment mixture would be needed in order to match the original color
- With Raman spectroscopy, paints can be analyzed without damaging priceless works of art
- In the above paper over 170 pigments from important paintings and paints were analyzed in order to develop a reference guide to be used for restorations.

In the above figure, a paint sample from a notable painting was analyzed through Raman and matched to a pigment present in the database they developed. It also shows the FTIR spectra of the same unknown paint and its pigment match, demonstrating the superiority of Raman to be used in this kind of analysis.

The above table is an example of the library developed using Raman spectroscopy. The notable peaks were marked and bolded to help differentiate between similar structures. Raman spectroscopy has very little noise and produces bands that are narrow enough to differentiate between the second and fourth structures, even though they only differ by two C-Cl bonds, by identifying the single very strong peak at 1337 on the fourth structure.

### Works cited

<https://www.slideshare.net/wilsonJefrijanto1/raman-spectroscopy-58655569>

[http://www.kosi.com/na\\_en/products/raman-spectroscopy/raman-technical-resources/raman-tutorial.php](http://www.kosi.com/na_en/products/raman-spectroscopy/raman-technical-resources/raman-tutorial.php)

<http://www.inphotonics.com/raman.htm>

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## Solid-state nuclear magnetic resonance spectroscopy (Solid-state NMR)

Student authors: Huiyan Anna Xiong and Kathy Stepien 2020

### How solid-state NMR works

In NMR spectroscopy, the resonance frequencies of nuclei are measured in the existence of an applied magnetic field (usually represented as  $B_0$ ). Solid-state NMR is similar to solution-state NMR but the sample is solid instead of solution. For solution state NMR, chemical shift and J-coupling (spin-spin splitting) are the interactions basically influence the resulting spectra. Two other interactions, the  $^1\text{H}$ - $^{13}\text{C}$  dipole-dipole couplings and chemical shift anisotropy (CSA), are averaged in solution-state NMR due to the rapid tumbling of the molecules in solution. In other words, both interactions were related to the orientation of molecules. However, molecules in solids don't tumble a lot and the direction matters. So both of the interactions have significant effect in the solid-state NMR, which results in much more broad peaks instead of narrow peaks in solution-state NMR.

To gain solid-state NMR spectra with higher resolution, additional hardwares needs to be used, such as magic-angle spinning (MAS) which spins the sample rapidly at an angle of  $54.7^\circ$  with respect to the external magnetic field and averages the chemical shifts to their isotropic value (Figure 1 a compared to c). <sup>1</sup> The rate of MSA needs to be greater than (or equal to) the magnitude of the anisotropic interaction to average it to zero. As well as it enhances the resolution of solid-state NMR, the MAS may lead to the presence of spinning sidebands as shown in Figure 1 b, e and f. <sup>1</sup> These are spurious signals (i.e. peaks) that result from the modulation of the magnetic field at the spinning frequency. The peaks always appear on either side of any large genuine peak at a separation of integer multiples to the spinning rate. The intensity of these sidebands will be proportional to the intensity of the genuine peak. Thus if the spin rate is 20 revolutions/second (= 20 Hz), you would look for spinning sidebands at frequencies  $20n$  Hz ( $n$  is an integer) above and below the resonance frequencies of genuine signals.

Figure 1 link: <https://pubs.acs.org/doi/10.1021/ac504288u>

### How do you interpret a solid-state NMR spectrum?

The principles behind solid-state NMR are similar to those of liquid-state, and it is a useful method of characterization when a sample cannot be dissolved in solution. The peaks tell us about the chemical environment that a specific type of proton exists in. Similar to liquid-state NMR where the instrument can identify  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , etc., solid-state NMR is capable of looking at the same types of nuclei, however the  $^1\text{H}$  NMR generally displays a broad, featureless peak, that is challenging to interpret ([Western Science](#)). The methods used in analyzing liquid-state NMR can also be applied to solid-state. If multiple nuclei are present in a compound in equivalent chemical environments, they will appear as one peak in the spectrum. Multiple peaks will be seen when the nuclei exists in more than one environment. The ideas of multiplicity and integration can also be applied. Solid-state NMR is valuable because it can also provide information beyond that of liquid-state. For example, dipole-dipole couplings can show the spatial arrangements of atoms. Relaxation times can tell us about system dynamics, like if the compound is in a porous media ([Pines Lab Berkeley](#)). The shape of the peak relates to the environment the nuclei exist in. The following image shows an example of how the peak shape changes in  $^{13}\text{C}$ -NMR from three different symmetries:

([Rossum 2011](#))

### What are good literature examples?

Link to the paper: <https://pubs.acs.org/doi/10.1021/cm900129u>

Figure 5.  $^7\text{Li}$  NMR MAS (10 kHz) spectra of LLTO powder after synthesis (a), after exchange in water at  $25^\circ\text{C}$  for 24 h (b), and after exchange in water at  $70^\circ\text{C}$  for 24 h (c). Spectra have been normalized to the powder weight. The insert shows the reconstruction of curve (a). \* is for impurity (1% of lithium total). <sup>2</sup>

### What are useful resources for in-depth reading?

Some potentially useful books on solid state NMR include:

1. Introduction to Solid-State NMR Spectroscopy | Wiley <https://www.wiley.com/en-us/Introduc...-9781405109147> (accessed Feb 13, 2020).
2. *Solid-State NMR Spectroscopy Principles and Applications*; Duer, M. J., Ed.; Blackwell Science Ltd: Oxford, UK, 2001.
3. *Solid State NMR*; Chan, J. C. C., Ed.; Topics in current chemistry; Springer Berlin Heidelberg: Berlin, Heidelberg, 2012; Vol. 306.

[https://en.Wikipedia.org/wiki/Solid-state\\_nuclear\\_magnetic\\_resonance](https://en.Wikipedia.org/wiki/Solid-state_nuclear_magnetic_resonance)

[http://www.emory.edu/NMR/web\\_swu/SSNMR\\_redor/ssnmr\\_schurko](http://www.emory.edu/NMR/web_swu/SSNMR_redor/ssnmr_schurko)

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(2) Boulant, A.; Maury, P.; Emery, J.; Buzare, J.-Y.; Bohnke, O. Efficient Ion Exchange of  $\text{H}^+$  for  $\text{Li}^+$  in  $(\text{Li}_{0.30}\text{La}_{0.57}\text{□}_{0.13})\text{Tio}_3$  Perovskite in Water: Protons as a Probe for Li Location. *Chem. Mater.* **2009**, *21* (11), 2209–2217.

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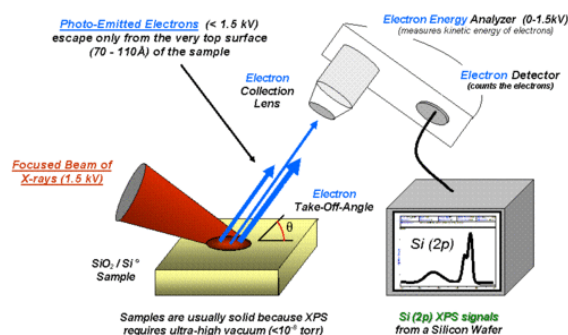


## X-ray Photoelectron Spectroscopy (XPS)

Student authors: Crystal Good 2018 & Horace Facey 2019

### How XPS works

X-rays (photons) are shot onto a sample, and when electrons in the sample absorb enough energy, they are ejected from the sample with a certain kinetic energy. The energy of those ejected electrons is analyzed by a detector and a plot of these energies and relative numbers of electrons is produced. Electrons of different energies follow different paths through the detector which allows the computer to differentiate the electrons and produce the spectra seen below.



**Figure 1:** Diagram depicting the instrumentation of the X-ray photoelectron spectrometer.

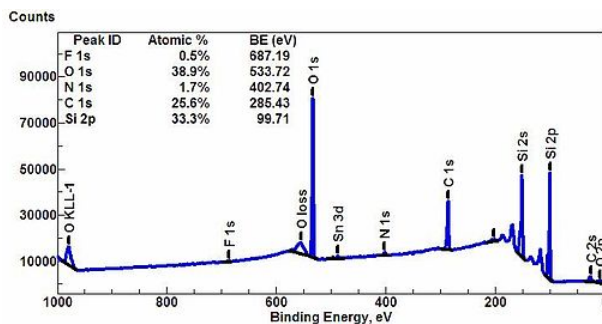
(Image released to public domain. Source: [https://en.Wikipedia.org/wiki/X-ray\\_...n\\_spectroscopy](https://en.Wikipedia.org/wiki/X-ray_...n_spectroscopy))

Atoms present in compound being tested by XPS are determined according to the equation:

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)$$

Here, binding energy is the energy of an electron attracted to a nucleus; photon energy is the energy of X-ray photons being used by the spectrometer, and the kinetic energy is the energy of the ejected electrons from the sample. The work function is a correction factor for the instrument and correlates to the minimum energy required to eject an electron from an atom (see the photoelectric effect for more info, but not necessary to understand this). The work function and photon energy are known and the kinetic energy is measured by the detector. That leaves the binding energy as the only unknown, which can then be determined. As electrons are in orbitals farther from the nucleus, less energy is required to eject them, so the binding energy is lower for higher orbitals. Electrons contained in different subshells (s,p,d, etc.) have different energies as well. By showing the energy of electrons emitted from a material, XPS allows for the composition of a material to be determined.

Additionally, chemical shifts can be determined using XPS. This is owing to the fact that binding energy doesn't only depend on the shell of the electron. It also depends on the environment, that is, the bonds that the atom in question partake in. Therefore, a primary carbon would have a slightly different binding energy than a carboxyl carbon, for example.



**Figure 2:** XPS spectra. Graph showing the binding energies of electrons from different orbitals (F1s, O1s, Si2p, etc.) and their intensities which tell the atomic composition of the sample based on the amounts of each electron from different orbitals present.

(Figure courtesy of the creative commons license. Source: [https://en.Wikipedia.org/wiki/X-ray\\_photoelectron\\_spectroscopy](https://en.Wikipedia.org/wiki/X-ray_photoelectron_spectroscopy)).

## How to interpret the data it generates

1. Peaks from the XPS spectra give relative number of electrons with a specific binding energy. The shorter the peak, the less electrons represented. For example, if a peak *A*, is half the height of another peak *B*, that means there were half as many electrons detected with the binding energy at *A* compared to the number of electrons detected with the binding energy at *B*. Therefore, the peak intensities give information about the percent composition of a material. As seen in the figure above, the O1s has the largest peak, and it shows that the atomic composition of oxygen is the greatest.
2. The greater the binding energy, the greater the attraction of that electron to the nucleus. i.e. peaks from electrons in 1s will have a greater energy than peaks representing electrons from 2s. Electrons in 2s will have greater energy than those in 2p. Some instruments have peak identification features, but otherwise, the identification of peaks/lines on the spectra can be completed by looking at standards of different materials. Moulder (1992) shows examples of these standards to help interpret the spectra.

## Error/difficulties in reading the spectra

1. Be careful about the direction of the scale for binding energy. There are examples figures having zero is on the left and some having it on the right.
2. Some lines/peaks may overlap, making it difficult to determine if the electrons represented are coming from different atoms
3. Auger lines: lines with complex patterns, not related to the kinetic energy from ionization of electrons. It is important to identify these lines first.
4. X-ray ghost lines: small lines or peaks that are shifted a little more than expected due to additional x-ray sources than from the instrument
5. Only the surface is tested, so the behavior at the surface and bulk may be quite different.

## Good literature examples

Penke, Y.K.; Anantharaman, G.; Ramkumar, J.; Kamal, K. "Aluminum Substituted Cobalt Ferrite (Co–Al–Fe) Nano Adsorbent for Arsenic Adsorption in Aqueous Systems and Detailed Redox Behavior Study with XPS." *ACS Appl. Mater. Interfaces*. 2017, 9, 11587–11598.

This paper discusses the adsorption of arsenic into aluminum substituted cobalt ferrite. XPS is used to confirm the presence of Al, and then the instrument confirms the oxidation or reduction of arsenic when it is adsorbed into the material.

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- <https://www.youtube.com/watch?v=2h6GeXrfGzY>

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## CHAPTER OVERVIEW

### Thermal Analysis

Differential scanning calorimetry (DSC) (empty)

Thermogravimetric analysis (TGA)

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## Differential scanning calorimetry (DSC) (empty)

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## Thermogravimetric analysis (TGA)

Student authors: Luis F. Garcia-Herrera & Henry Price 2020

### How TGA works

In thermogravimetric analysis (TGA), a sample is continually weighted while heating, as an inert gas atmosphere is passed over it. Many solids undergo reactions that evolve gaseous byproducts. In TGA, these gaseous byproducts are removed and changes in the remaining mass of the sample are recorded. Three variations are commonly employed:

- Dynamic TGA - Temperature continues to increase over time as mass is recorded. This allows simultaneous identification of how much gas is removed and the temperature at which it occurs.
- Static TGA - Temperature is held constant as the mass is measured. This can be used to gain more information on a decomposition that happens at a certain temperature or to investigate a material's ability to withstand a given temperature.
- Quasistatic TGA - Sample is heated in multiple temperature intervals, and held at those intervals for a time, often until the mass stabilizes. This is ideal for investigating substances that are known to decompose in various ways at different temperatures, and better characterizing the way in which they decompose.

### How to interpret the data

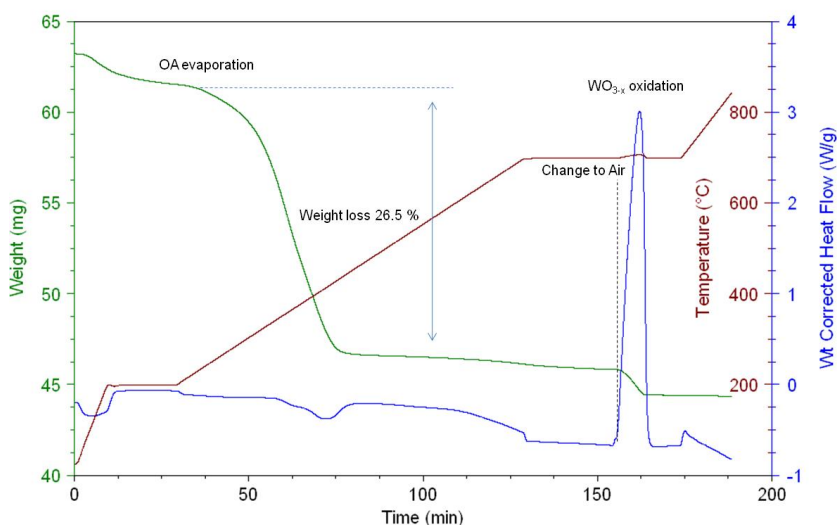


Figure 1 shows a TGA curve in green. Figure from [Physical Methods in Chemistry and Nanoscience](#) by Pavan M.V. Raja and Andrew R. Barron ([chemlibretext link](#)).

Data from thermogravimetric analysis is often shown by a graph representing mass as a function of temperature for dynamic TGA. For static TGA, mass is instead plotted as a function of time at a given temperature. Quasistatic TGA produces multiple mass vs. time plots for various temperatures. The derivative of the mass change with temperature is often plotted on the same graph to improve ease of identifying the points at which different mass changes occur; especially helpful in cases where multiple decomposition reactions happen in close proximity to one another.

Examples of some characteristic TGA curves for dynamic TGA

**Figure 1.** Classification of the different observable TGA Curves. [Image source](#)

In general, mass fluctuations correspond to chemical reactions, with some exceptions. A common example is drying, which can easily be seen as a quick initial drop at the beginning of heating that isn't known to correspond to any chemical reactions. Evaporation/sublimation may also appear on the plot depending on the material to be analyzed. Multistage decomposition is also common, and shows as a step-like pattern. In some cases, these steps may blend together during dynamic TGA, necessitating either far slower heating rates, or step-wise methods like quasistatic TGA. Note that TGA itself may not be sufficient to identify the decomposition products; chemical testing of the sample after TGA analysis is often required to ascertain the identities of suspected

decomposition products. TGA itself does not identify substances; other methods such as chemical testing or differential calorimetry must be performed alongside TGA to verify the identity of products.

### Good literature examples

TGA is vital when designing materials that are intended to withstand high temperatures, as if there is even slight decomposition of the material at a temperature that the material would be expected to encounter, devices made of the material may fail over repeated use. The carefully controlled environment of the TGA analyzer also allows for measuring decomposition reaction kinetics. Differential scanning calorimetry can be incorporated into the TGA analyzer to allow for monitoring potential phase changes. Phase changes generally require addition of heat, yet do not increase the temperature of the sample undergoing a phase change. Furthermore, different phases of a material have different heat capacity, and the temperature change per joule of heat applied will vary with phase. By adding a reference pan to the TGA analyzer, changes in the heat capacity in addition to mass changes can be monitored. In this way, both phase changes and thermal decomposition reactions can be simultaneously measured by TGA.

TGA used for decomposition reaction:

**Figure S6.** Thermogravimetric analysis (TGA) under pure nitrogen flow at 100 mL/min to show a) clean decomposition of 3DP-HKUST-1gel and b) decomposition of 3DP-HKUST-1gel/TEA showing that it has several side products during decomposition. ([Lim et al. 2019](#))

**Figure 2b.** Thermogravimetric analysis (TGA) under simulated ambient conditions (SI section 5), showing desolvation followed by oxidation of 3DP-HKUST-1gel to CuO.

The authors are looking to use colloidal gels containing only ethanol and  $\text{Cu}_3(\text{BTC})_2$  (BTC = 1,3,5-benzenetricarboxylate) (HKUST-1) nanoparticles as ink for the direct ink writing (DIW) of pure densely packed and self-standing Metal-organic frameworks (MOF) monoliths. Traditionally they are synthesized in powder form. The authors are observing the decomposition behavior of the 3DP-HKUST-1gel (made using DIW) and 3DP-HKUST-1gel-TEA (made by triethylamine-induced HKUST-1 gels). It can be observed in the sudden change in weight over the 100-200 °C for **Figure S6b** that several side products have formed as opposed to **Figure S6a** which shows a much cleaner decomposition. The Figure seen in the paper was **Figure 2b**, the authors attribute the first weight change (16.2 mg) to residual molecules such as  $\text{H}_2\text{O}$ , acetate from the copper (II) acetate monohydrate precursor, and excess ethanolic solvent that is trapped inside the 3DP-HKUST-1gel structure. The second weight change (6.2 mg) was observed at 300 °C and is caused by the decomposition of the organic linkers and network.

### In-depth reading and works cited

1. [Physical Methods in Chemistry and Nanoscience](#) by Pavan M.V. Raja and Andrew R. Barron ([chemlibretext link](#)).
2. [A Beginners Guide Thermogravimetric Analysis \(TGA\)](#): A Beginners Guide to TGA that has FAQ and basic information.
3. [Thermogravimetry Analysis \(TGA\) – online training course](#): Youtube training course that has good explanation about how the TGA works. Also has good examples of plots and how to understand them.
4. [Thermogravimetric Analysis \(TGA\) & Differential Scanning Calorimetry \(DSC\)](#): Slideshow with information about the TGA. Includes figures on classification of curves, how balance works, analysis of curves, effects of heat rate, shifts caused by heat rate, etc.
5. [THERMAL ANALYSIS OF POLYMERS - Fundamentals and Applications](#): (WARNING!: This link will download a whole 388 pg. book!) Has a whole chapter dedicated to TGA.

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