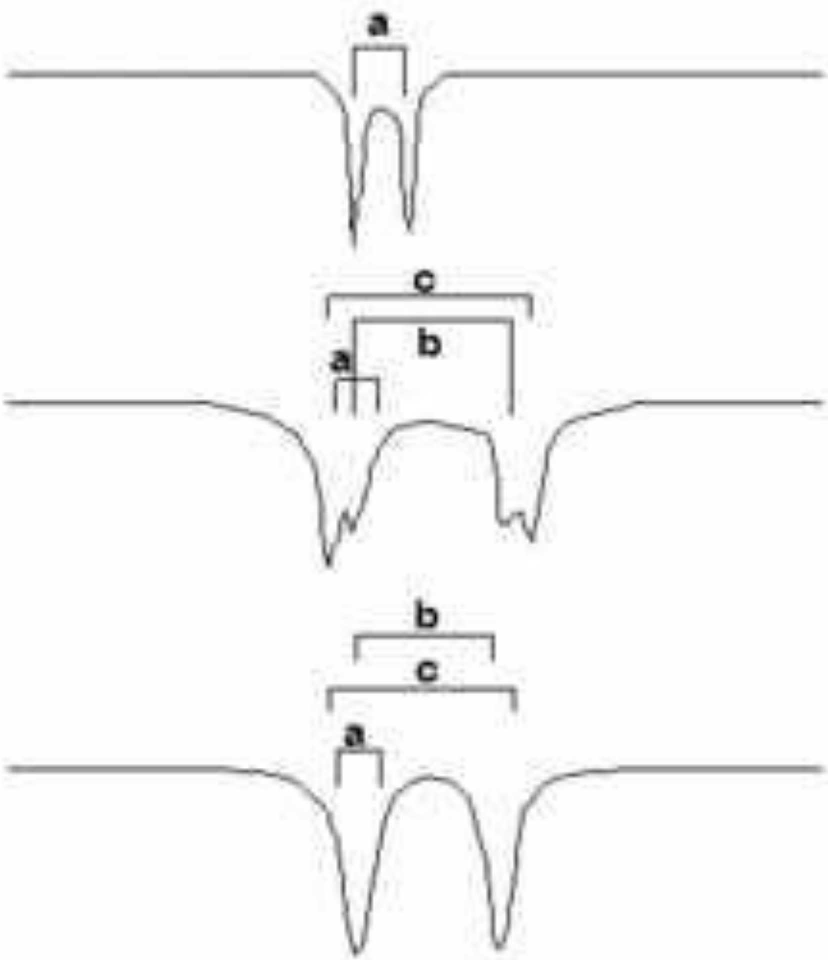
Fényképalbum13

szerző: PGY

Mössbauer spectroscopy



Spectra obtained from three coal samples.

a - iron pyrite
b - Fe^{2+} bearing clay
c - iron carbonate

Other Methods

There are many methods that do not fall into the class of nuclear activation or tracer technique.

We'll look at a few significant examples -but not in great detail.

- Particle-induced gamma ray emission (PIGE)
- Particle-induced X-ray emission (PIXE)
- Rutherford backscattering (RBS)
- Mössbauer spectroscopy

Ion beam analysis

Techniques that use ion beams as part of an analytical procedure.

Particle-induced gamma ray emission

Prompt γ method similar to NAA.

Particle-induced X-ray emission

Measures X-rays instead of γ.

Rutherford backscattering

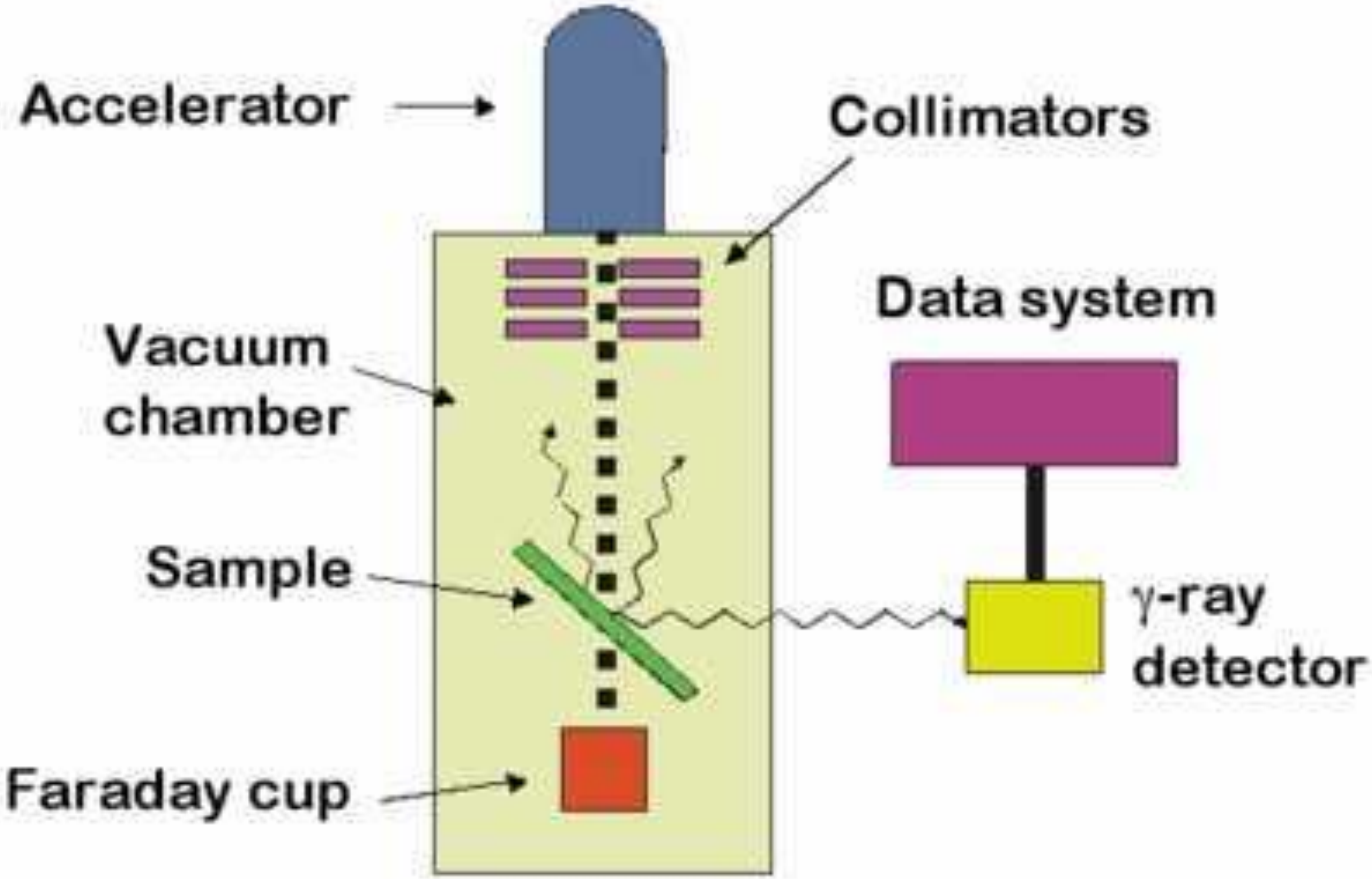
Measures the scattering of particles like α.

Particle-induced gamma-ray emission

PIGE

- With this method, the prompt γ emitted following a charged-particle induced nuclear reaction are detected.
- Both qualitative and quantitative information are obtained.
- It is analagous to prompt γ NAA.
- The approach is most useful for light elements ($Z<15$).

Particle-induced gamma-ray emission



Particle-induced gamma-ray emission

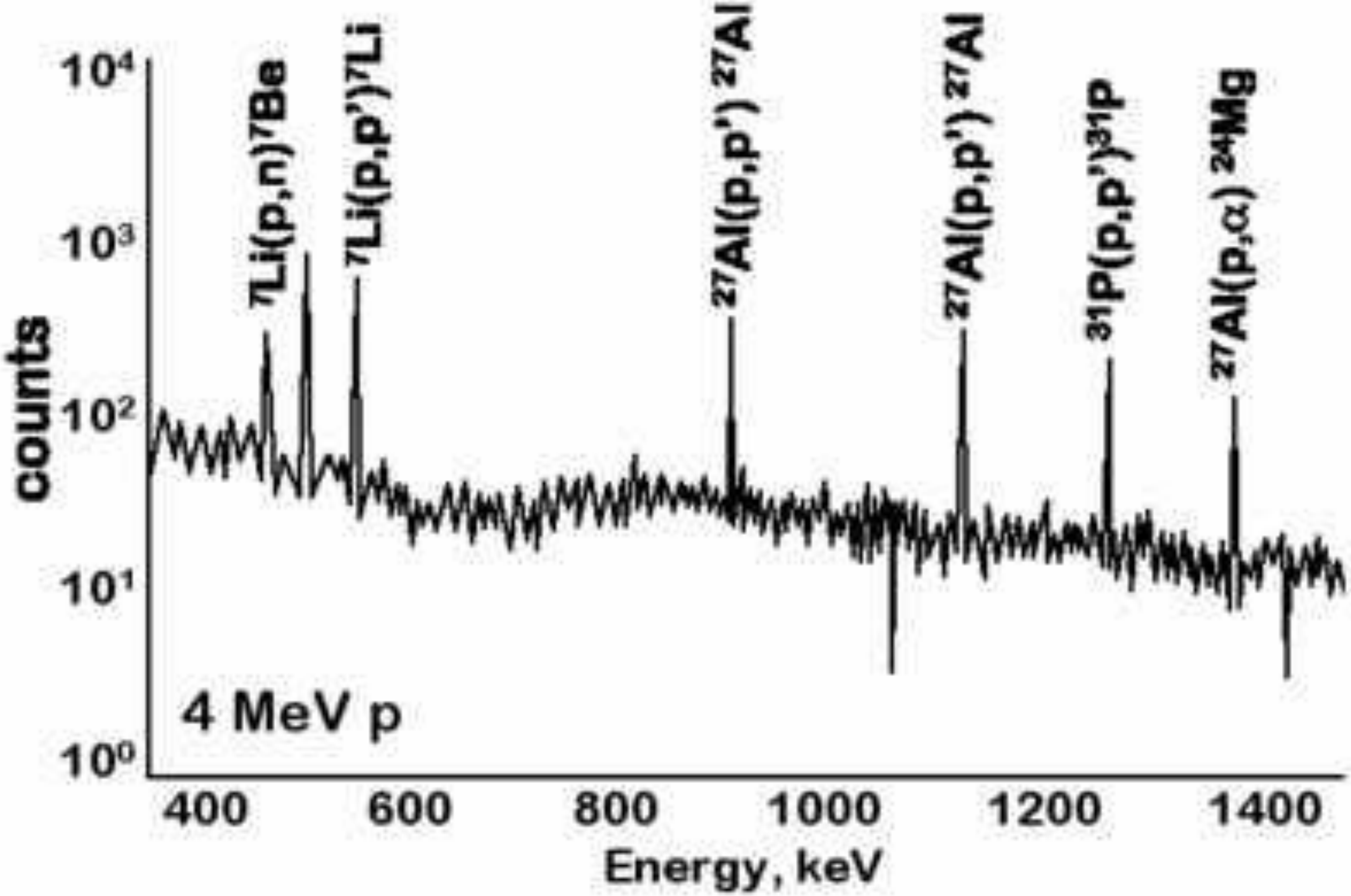
- ✓ The most common particle to use is the proton although deuterium, tritium, ^3He and α particles have been used.
- ✓ The method is used mainly to measure light elements on surfaces or thin films.
- ✓ Depth and surface profiling is possible by rastering the beam.
- ✓ It is commonly used along with PIXE since the methods use similar equipment.

Particle-induced gamma-ray emission

Element	Reaction	Product $t_{1/2}$	γ MeV
Boron	$^{11}B(p,n)^{11}C$	20.3 m	0.511
	$^{10}B(p,n)^{7}Be$	53.28 d	0.478
Carbon	$^{12}C(d,n)^{13}N$	9.97 m	0.511
Nitrogen	$^{14}N(p,\alpha)^{11}C$	20.3 m	0.511
	$^{14}N(p,n)^{14}O$	70.6 s	2.31,0.511
Oxygen	$^{16}O(p,\alpha)^{13}N$	9.97 m	0.511
Phosphorus	$^{31}P(\alpha,n)^{34m}Cl$	32.2 m	2.13, 1.18

0.511 values are actually due to β^+ annihilation energy.

Particle-induced gamma-ray emission



Particle induced X-ray emission

PIXE

- Particles produced by an accelerator or by nuclear decay are used for electron excitation of a sample.
- The most common particle to use is a p.
- The method is often classified as a nuclear method although the interaction is electronic.
  - X-ray emission.
  - Subatomic particles are used for excitation.

Particle induced X-ray emission

Why bother? Other methods of producing X-rays are much simpler.

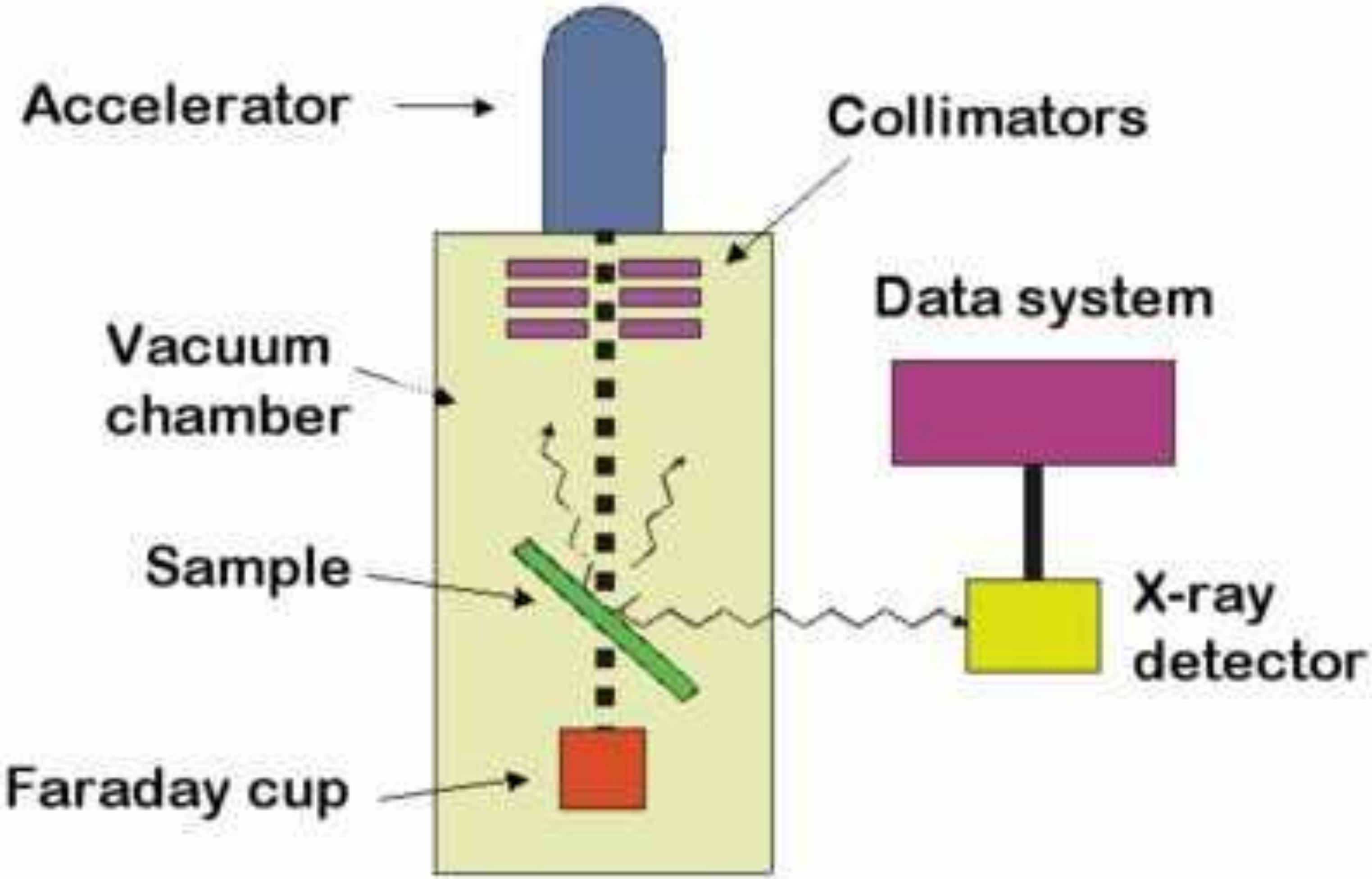
- Protons, being heavier particles, produce much less background bremsstrahlung radiation. Better sensitivity results.
- Protons can be focused over a much smaller area, permitting spatial resolution.
- Depth profiling is possible by varying the energy of the protons.

PIXE equipment

Near identical to PIGE.

- Van de Graaff or Cockroft-Walton accelerators are used to produce proton beams of a few nanoamperes - measured using a Faraday cup.
- A collimator is used to insure a parallel beam of protons -- typically made of graphite.
- Vacuum - 10^{-6} torr.
- Detector - Si(Li).

Particle induced X-ray emission



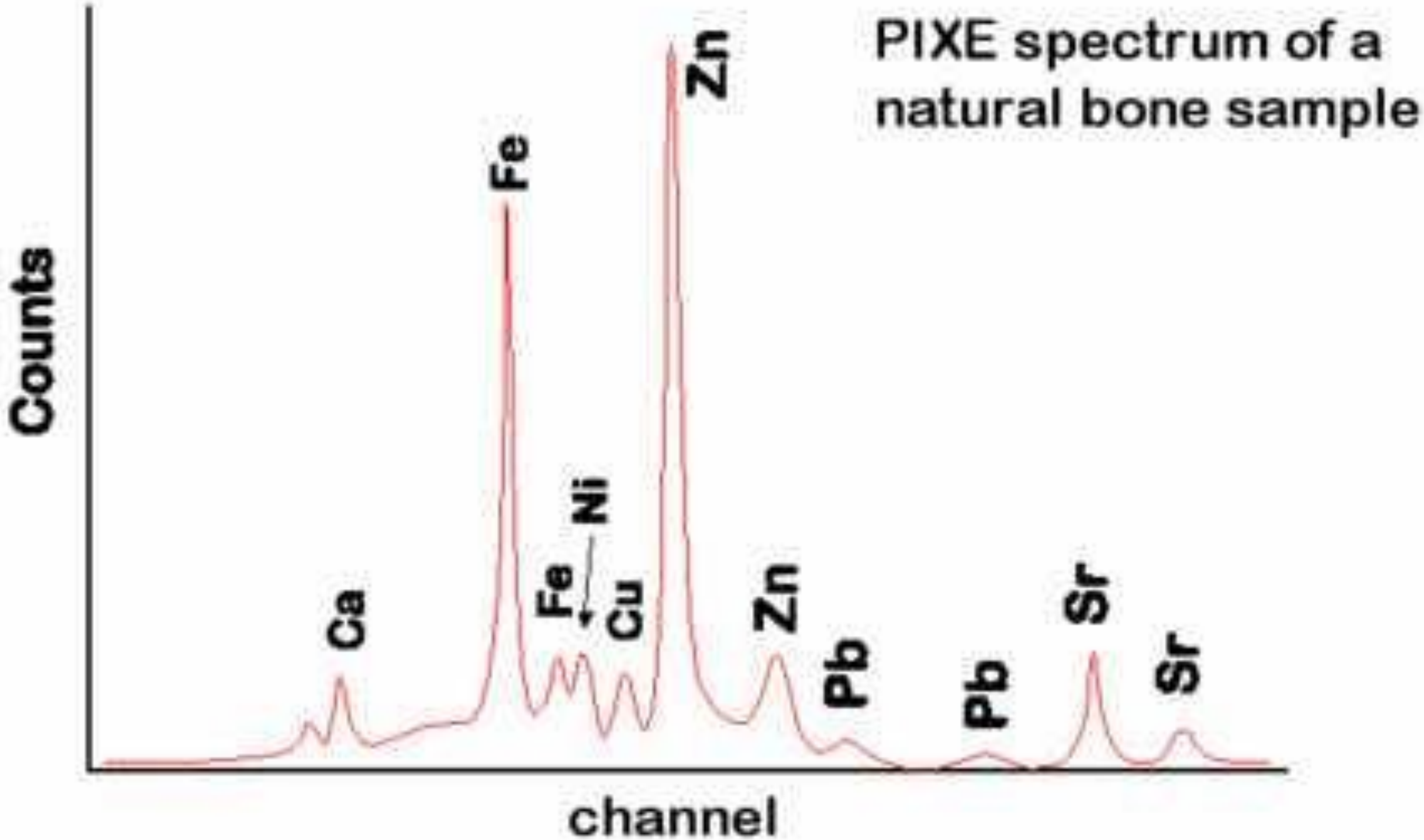
Particle induced X-ray emission

One major problem is the need to 'break vacuum' in order to change the sample.

- Several types of sample holders have been evaluated that contain several samples.
- One type is a 'ladder' that can be moved from 'rung' to 'rung' to change samples.

Samples must be either be rigid (bone, hair, minerals,...) or be mounted on a support.

Particle induced X-ray emission



Particle induced X-ray emission

Recent examples of PIXE/PIGE applications.

Archaeology
- Pottery
- Stone artifacts

Art
- Paintings

Biology
- Spermatoza, teeth
- Phospholipid bilayers

Geology
- Volcanic aerosols
- Obsidian
- Zeolites

Industrial
- Borosilicate glass
- Waste waters

Particle induced X-ray emission

Micro-PIXE

- Proton beam is focused to a diameter much smaller that the 1 mm normally used.
- Spatial resolutions of 1μm can be achieved.
- This permits mapping of elements inside a single cell or mineral grain.
- Both qualitative and quantitative information can be obtained.

Rutherford backscattering

- The elastic scattering of charged particles by a target nuclei.
- It was this phenomena that Rutherford used in his early studies of atomic structure.

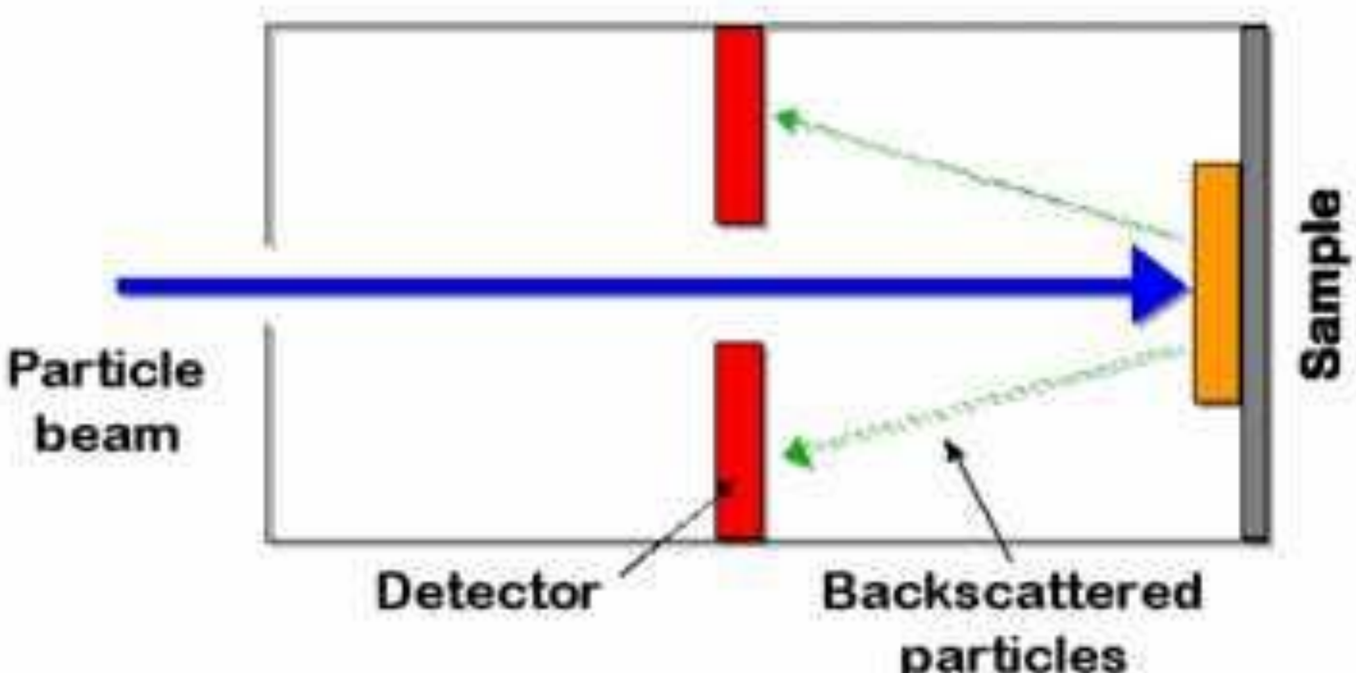
Rutherford backscattering spectrometry

- Surface/Thin film method
- Provides information about stoichiometry, structure, thickness and elemental concentrations.

Rutherford backscattering

Particle beam - α from accelerator
Detector - silicon surface-barrier

Entire system is under a vacuum.



RBS basis

- A particle with mass M_1 and energy E_0 hits a target with mass M_2, some energy is transferred.
- The particle (when scattered) will have less energy, E_1.
- The ratio of scattered to initial energy is:

$$K = \frac{E_1}{E_0} = \left[\frac{(M_2{}^2 - M_1{}^2 \sin^2\theta)^{1/2} + M1 \cos\theta}{M_2 + M_1} \right]^2$$

- If the mass of the projectile and the scattering angle are known, the mass of the target atoms can be determined.

RBS basis

Large scattering θ are preferred since they provides the best mass discrimination.

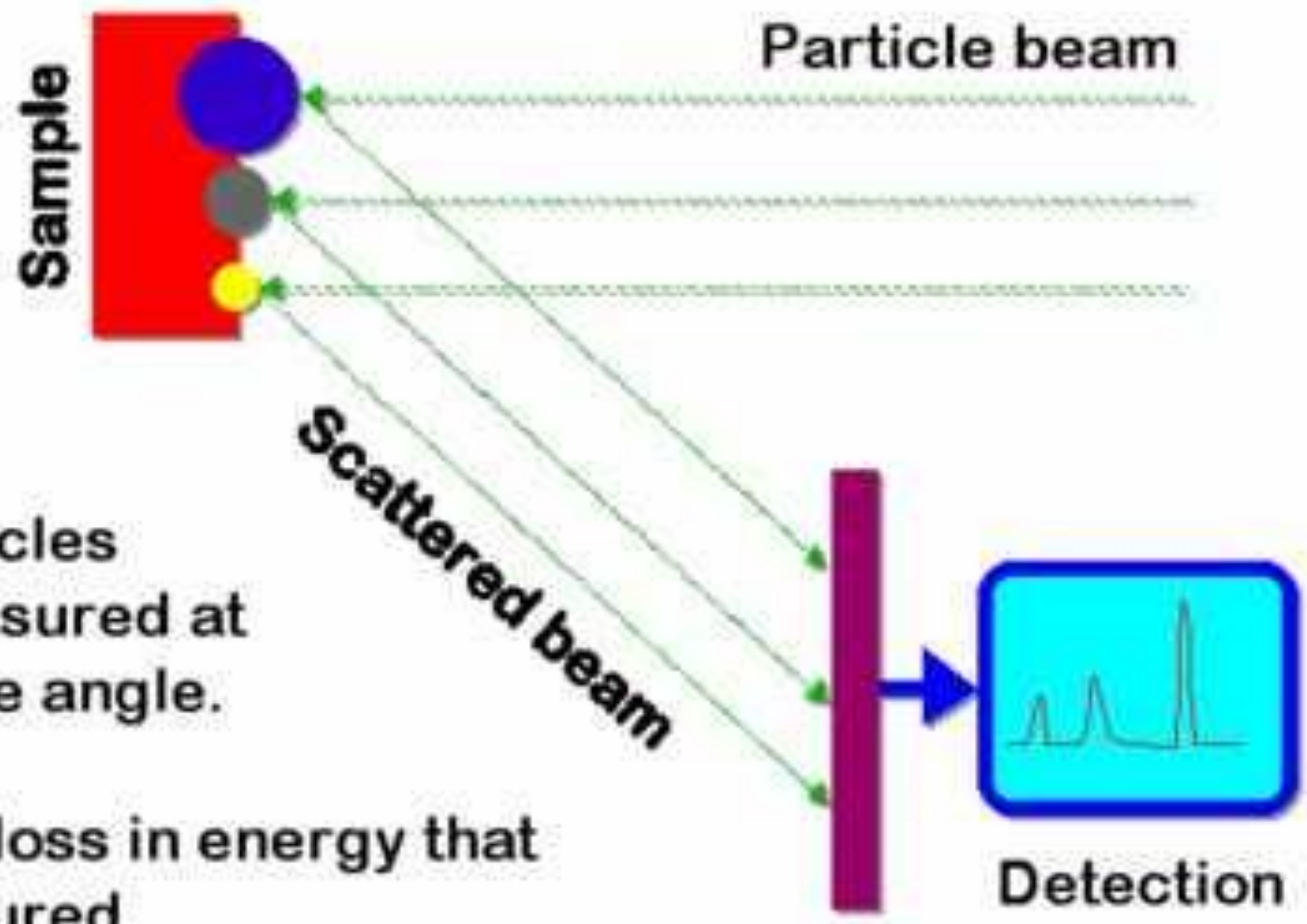
At 180° the equation simplifies to:

$$\frac{E_1}{E_0} = \left(\frac{M_2 - M_1}{M_2 + M_1}\right)^2$$

180° is not possible so 170° is common.

The method works best for heavy elements in a low mass matrix.

RBS surface analysis

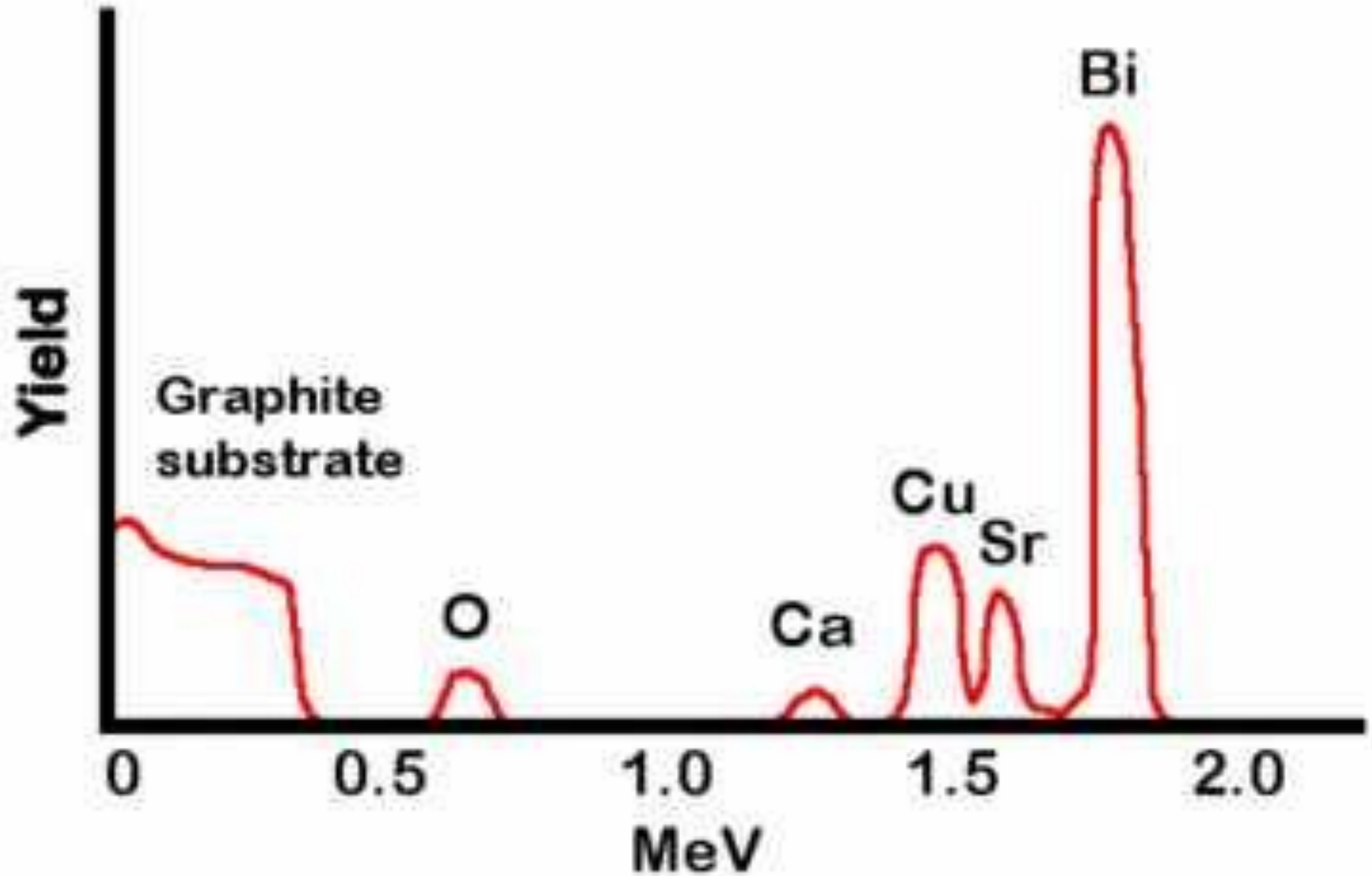


All particles are measured at the same angle.

It is the loss in energy that is measured.

Rutherford backscattering

α backscatter spectrum of a superconducting film.

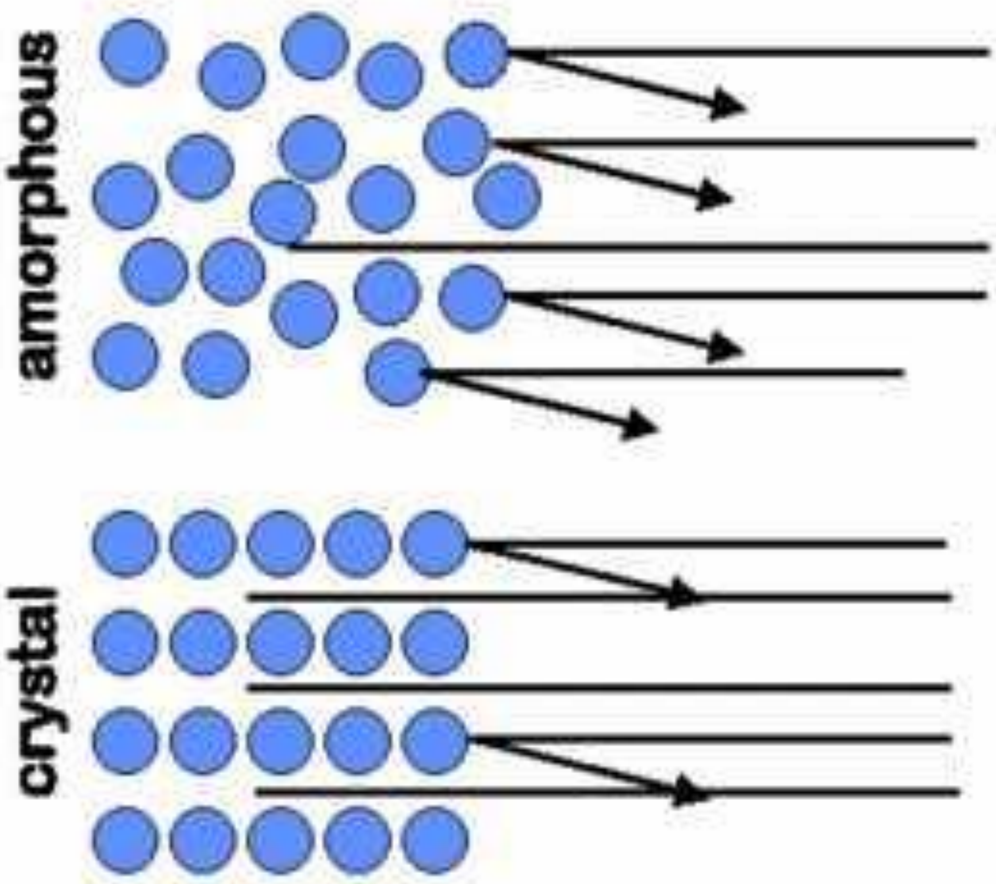


Channeling effects

Channeling

- Occurs in crystalline materials.
- Confinement of a particle beam within a given trajectory.
- If the particle beam is aligned with the crystal, there is a change in the degree of scattering.
- Provides information regarding crystal structure, defects and presence of impurities.

Rutherford backscattering



Mössbauer spectroscopy

Technique that relies on the recoilless resonance absorption of γ rays by nuclei.

Resonance absorption

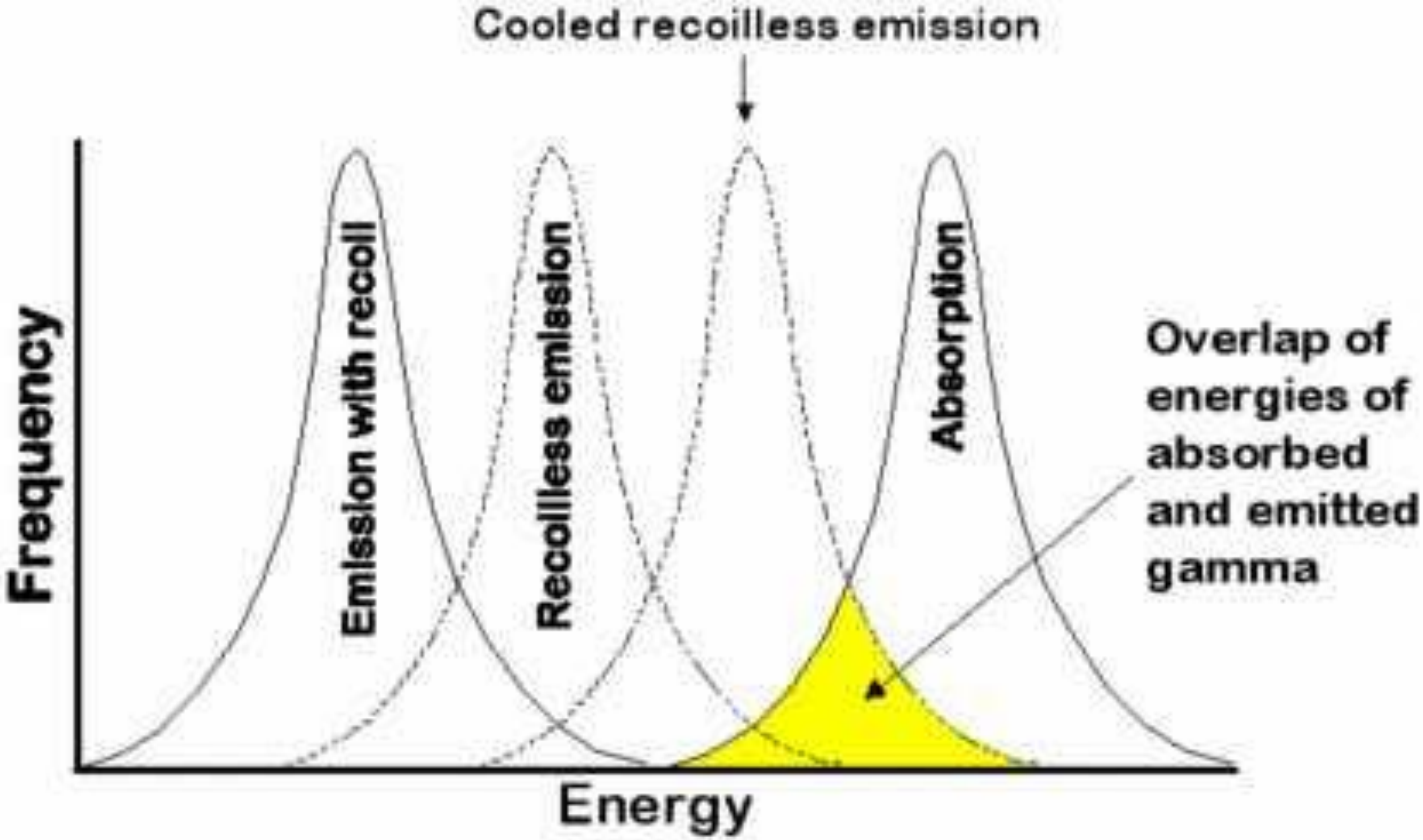
- **When a species emits and then reabsorbs radiation of the same energy.**
- **The source and sample must contain exactly the same radionuclide.**
- **The actual energy of absorption are affected by the chemical environment.**

Mössbauer spectroscopy

Recoil

- γ emitted by a nuclear decay will not be exactly the same as the energy for the nuclear transition.
- Some energy is lost due to the conservation of momentum.
- It is possible to minimize this loss by embedding the nucleus in a solid, crystalline material.
- Cooling the sample can further reduce recoil.

Mössbauer spectroscopy



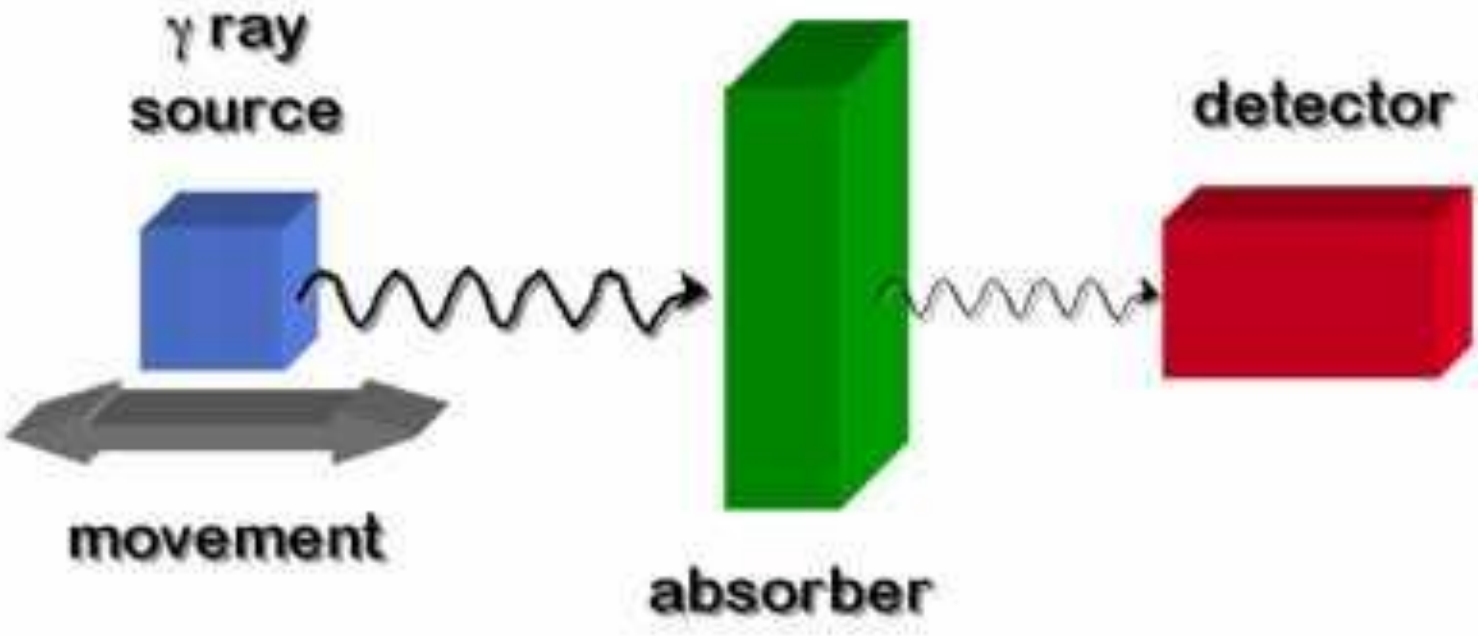
Mössbauer spectroscopy

So by properly preparing the sample and cooling it, we can get some overlap between emission and absorption.

We can also introduce small changes in the γ energy via the Doppler effect -- by moving the source with respect to the sample.

This allows for 'fine tuning' the emission energy to match absorption.

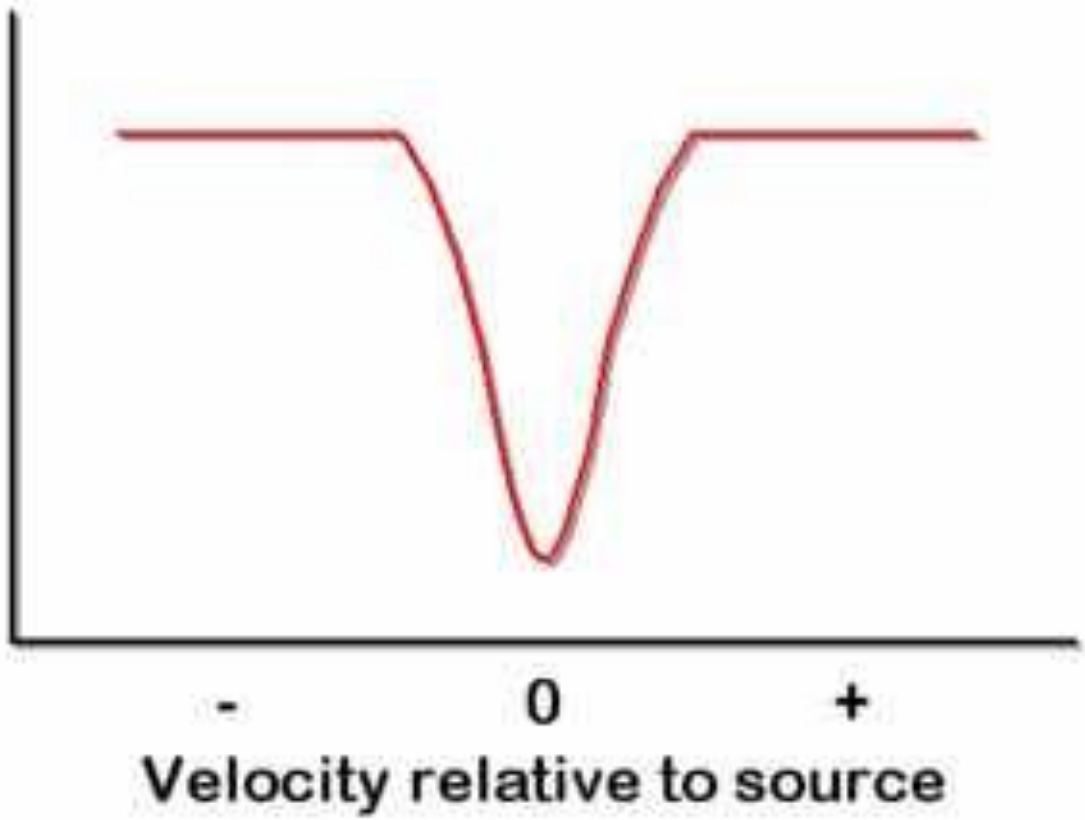
Mössbauer spectroscopy



Mössbauer spectroscopy

As the γ source is moved, the energy is varied. At some point, it matches the absorption energy of the target.

This is affected by the electronic (chemical) environment of the sample.



Mössbauer spectroscopy

Information about the sample is obtained using three hyperfine parameters.

Isomer (or chemical) shift

Difference in the transition energy of the source and target due to electron density at the nucleus.

This provides information about the valence state of the target.

Mössbauer spectroscopy

Other Hyperfine parameters

- Paramagnetic high-frequency interaction
- Quadrapole interactions

Cause splitting of the energy levels due to interactions between the electons and the magnetic and electric fields of the nucleus.

Information regarding charge symmetry, atomic configurations, metal bonds to ligands and solvent interactions can be obtained.

Mössbauer spectroscopy

The method is not applicable to all elements.

- Nuclei must have low-level excited states because the maximum g energy that can be effectively used is ~160keV.
- The half-life of the excited state must be in the 10^{-6}-10^{-10}s range.

^{57}Co has been the most commonly used radionuclide. It is used for studies of Fe.

Other systems include ^{119m}Sn-Sn, ^{191}Os-Ir, ^{153}Ba-Cs and ^{161}Tb-Dy.

Mössbauer spectroscopy

The transition with a $t_{1/2}$=1.0 x 10^{-7} s is what is used.