CHEM*3440

Chemical Instrumentation

Topic 13

X-Ray Spectroscopy

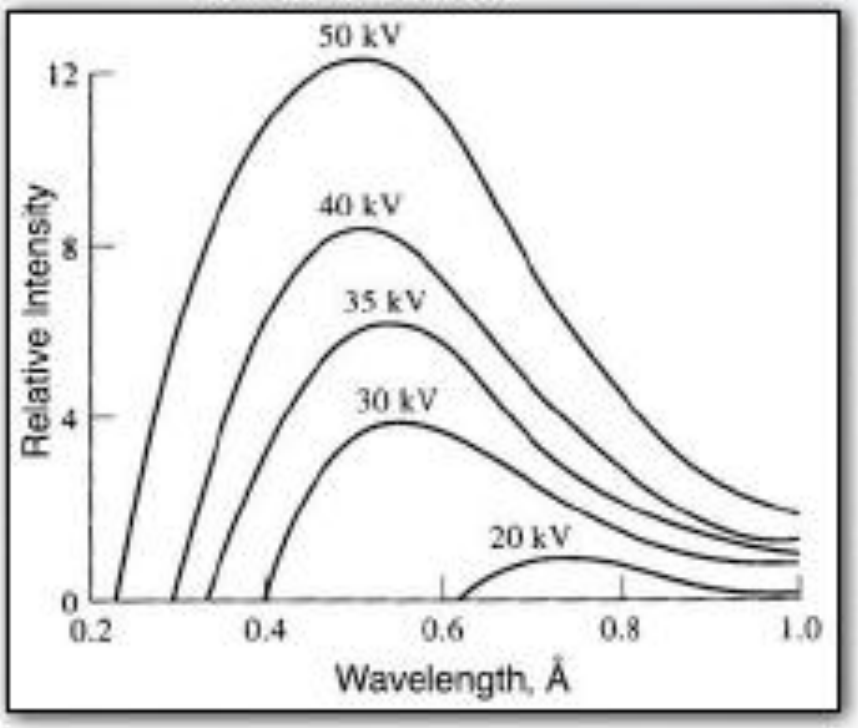
X-Ray Energies

- very short wavelength radiation 0.1Å to 10 nm (100 Å)
- Visible - Ultraviolet (UV) - Vacuum UV (VUV) - Extreme UV (XUV) - ***Soft X-ray*** - ***Hard X-ray*** - Gamma Ray
- often report photon energies, rather than wavelength. (above range is from 125 keV down to 125 eV)
- usually working in the range of a few keV.

Chemical bonds are in the range of 2 - 10 eV. An x-ray photon has LOTS of energy to break bonds; that's why they can be biologically damaging.

Bremsstrahlung Radiation

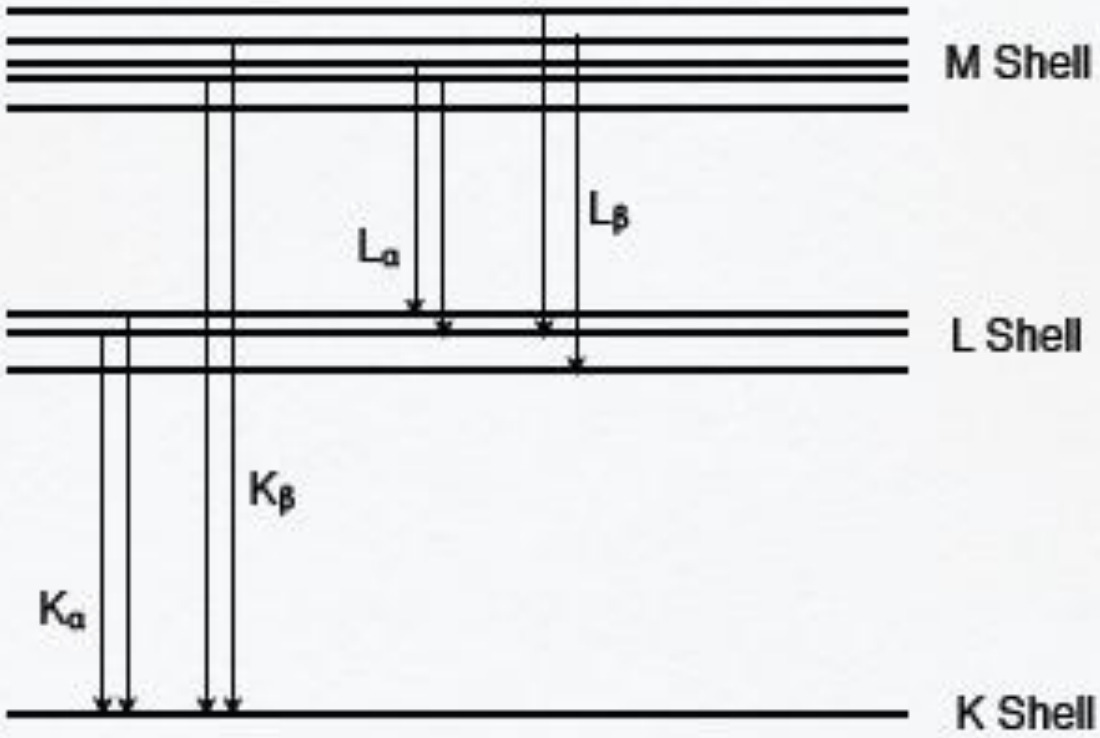
- this word is German for "braking"
- whenever a moving charged particle slows down rapidly, it emits photons commensurate with that kinetic energy loss. When high energy electrons crash into a solid target, they lose energy and emit continuum radiation in the x-ray region.



Note how the Bremsstrahlung envelope reaches to the energy of the electron beam accelerating voltage. Each electron is decelerated in a series of collisions, emitting an x-ray photon each time.

X-ray Line Spectra

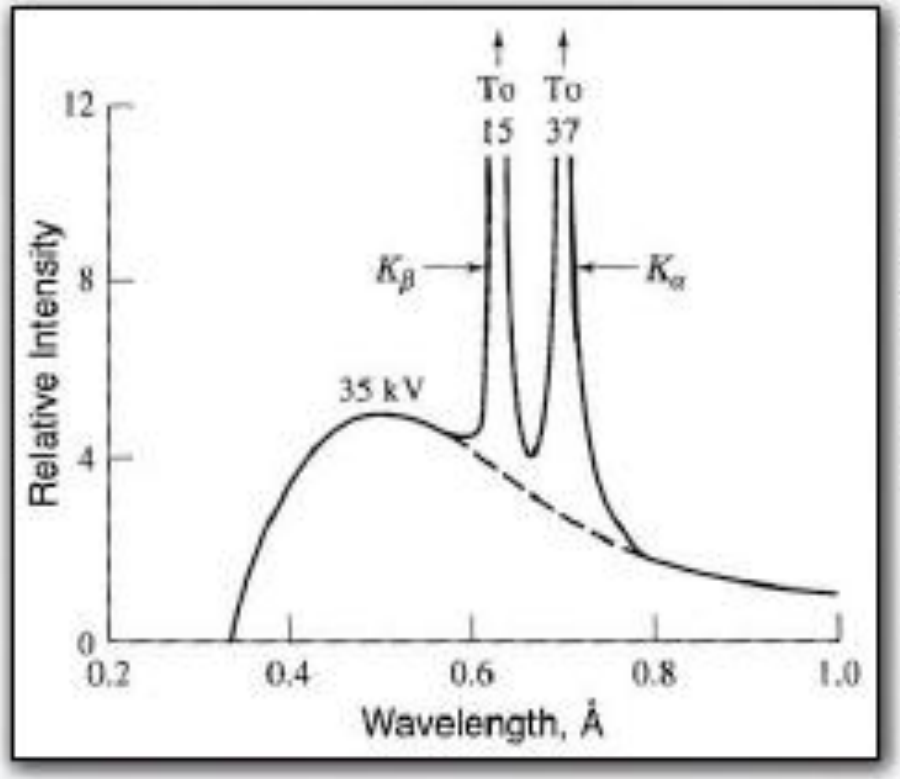
Atoms in excited states will lose energy by giving off photons. If that excitation is in the inner core levels, the energies of the emitted photons are in the x-ray regions.



Typical K and L Transitions

Element	Atomic #	K_α	K_β	L_α	L_β
Na	11	11.909 Å	11.617 Å		
		1041 eV	1067 eV		
Rb	37	0.926 Å	0.829 Å	7.318 Å	7.075 Å
		13380 eV	14946 eV	1693 eV	1751 eV
W	74	0.209 Å	0.184 Å	1.476 Å	1.282 Å
		59282 eV	67337 eV	8394 eV	9664 eV

Sources - Tubes

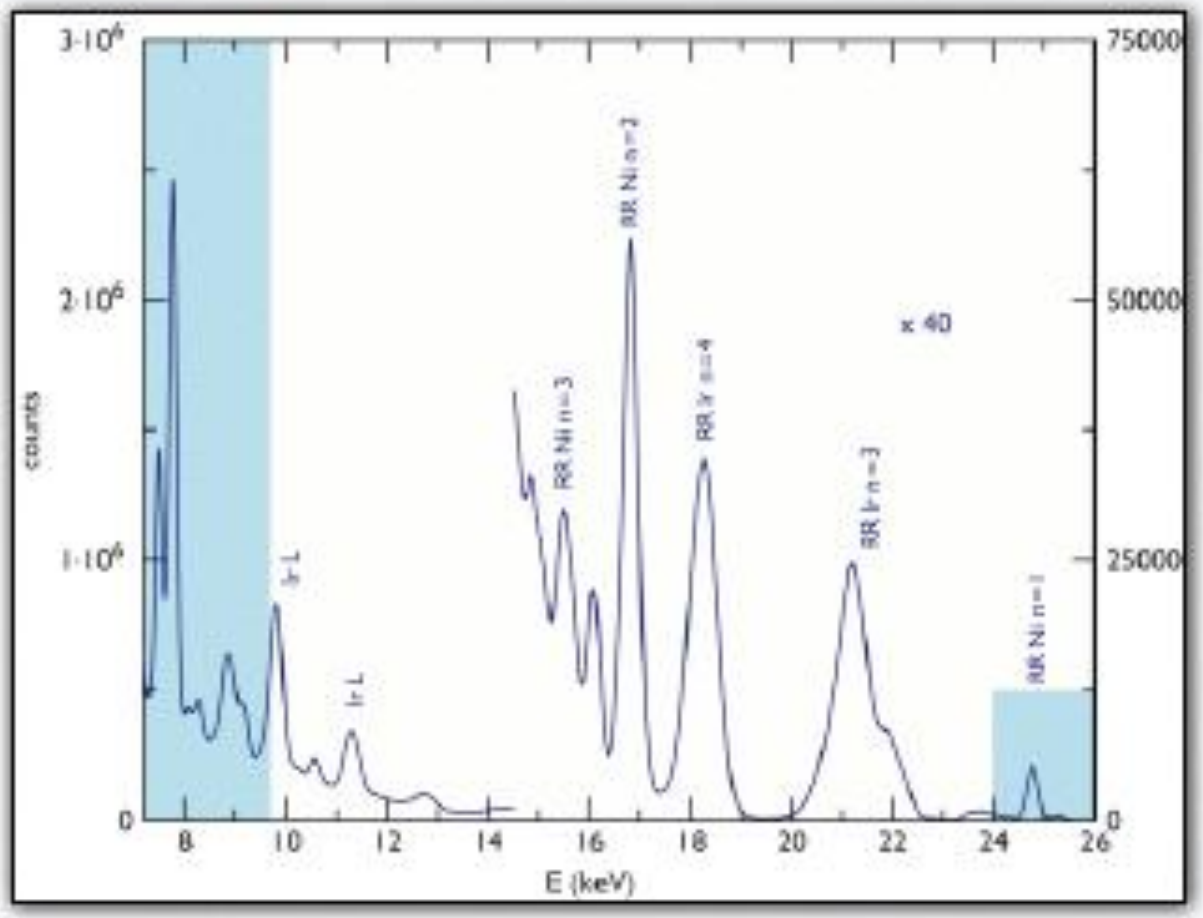


Most common x-ray source. Bombard a metal target with high energy electron beam. X-rays emitted are target atom's line spectrum imposed on top of Bremsstrahlung spectrum. <1% power goes into x-ray emission; balance heats target and it must be water-cooled. Acceleration voltage and beam current are critical parameters.

Sources - Fluorescence

If x-rays are used to irradiate another atomic target, the target re-emits its own x-ray spectrum. There is no Bremsstrahlung radiation in this case. Intensity is lower, but spectrum is "cleaner".

Ni X-ray Fluorescence Spectrum



Sources - Radioactive

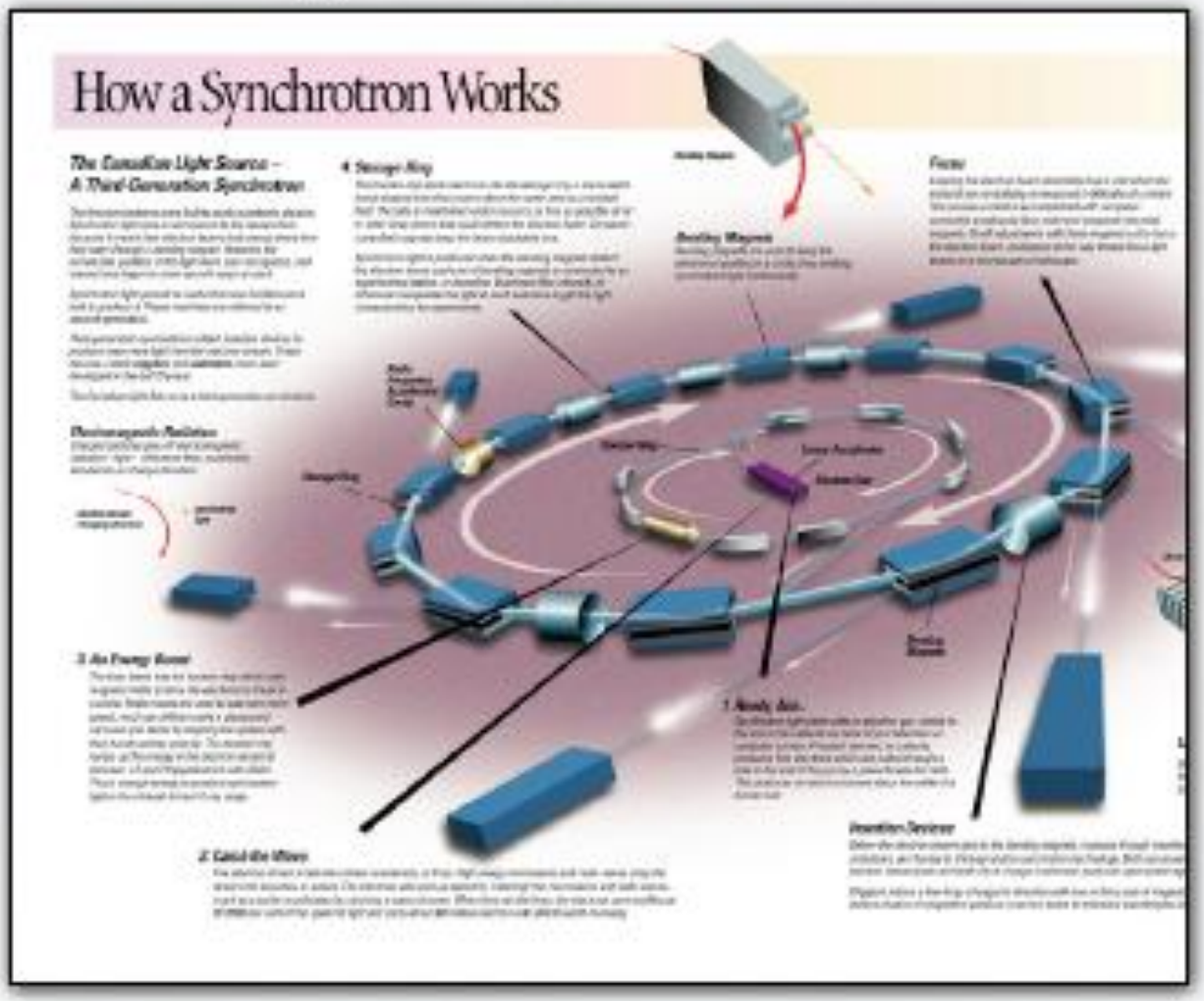
Various nuclear decay processes emits photons in the x-ray region. Can be sharp line emission (from electron capture decay processes) or continuum (from beta decay processes).

Useful as long lasting, low level sources of monochromatic x-rays.

$^{3}H \rightarrow {}^{3}He + e^{-}$	continuum radiation from 3 - 10 keV
$^{55}Fe + e^{-} \rightarrow {}^{54}Mn$	Mn K x-rays at 5.9 keV
$^{57}Co + e^{-} \rightarrow {}^{56}Fe$	Fe K x-rays at 6.4 keV
$^{109}Cd + e^{-} \rightarrow {}^{108}Ag$	Ag K x-rays at 22 keV
$^{210}Pb + e^{-} \rightarrow {}^{209}Bi$	Bi L x-rays at 11 keV

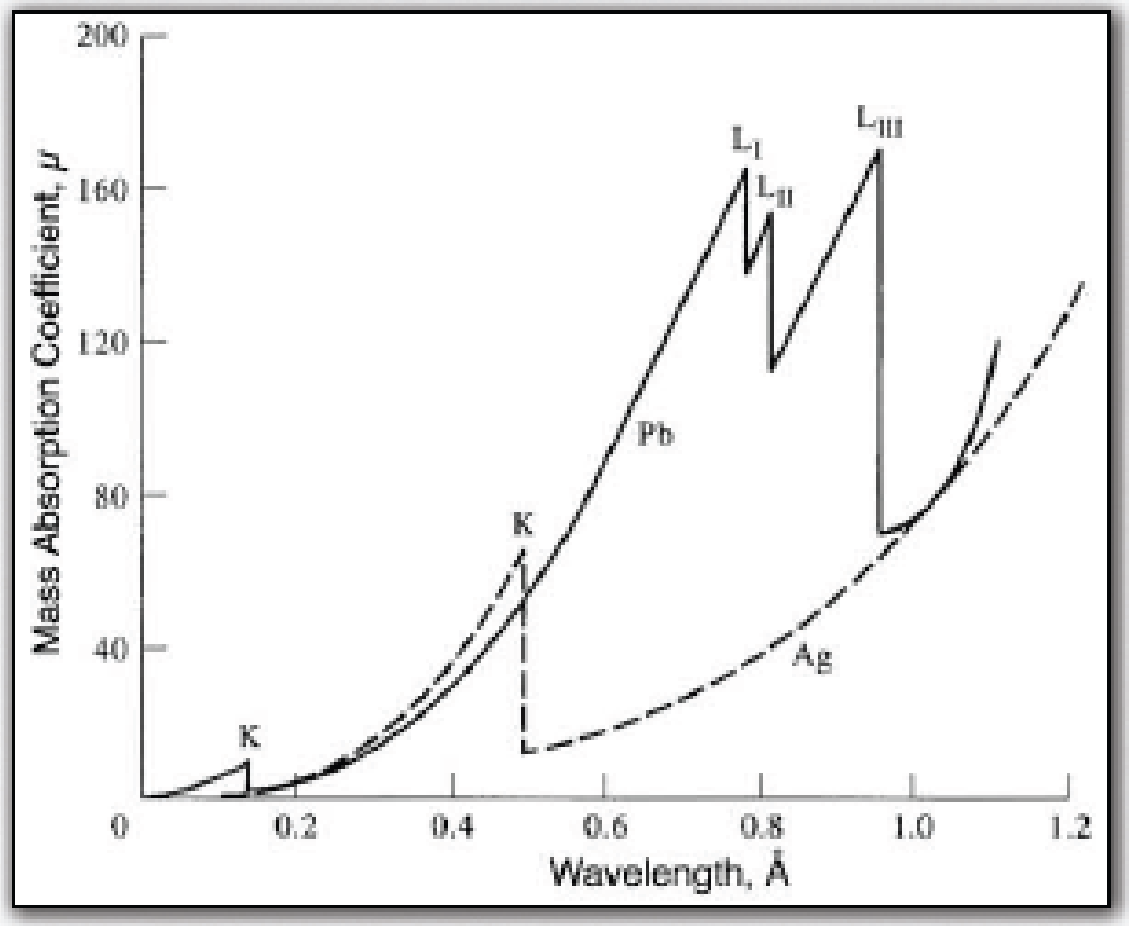
Sources - Synchrotron

The Canadian Light Source (CLS) in Saskatoon. Very important x-ray source; intense, continuously tunable, pulsed.



X-Ray Absorption

X-rays are absorbed when their energy matches the binding energy of an atom's electron. At higher energies, absorption still occurs, but with decreasing efficiency; excess energy shows up in kinetic energy of ejected electron (photoelectron). Absorption edges characterize x-ray absorption spectra.



Absorption Coefficient

Beer's Law applies to x-ray spectroscopy too. Written slightly differently.

- linear absorption coefficient μ

$A = \ln(P_0/P) = \mu x$

- mass absorption coefficient

$A = \ln(P_0/P) = \mu_m \rho x$

The mass absorption coefficient is independent of the chemical and physical state of the sample, but you must know the density (ρ) of the sample. The coefficient for a mixed sample is the weighted sum of the various components.

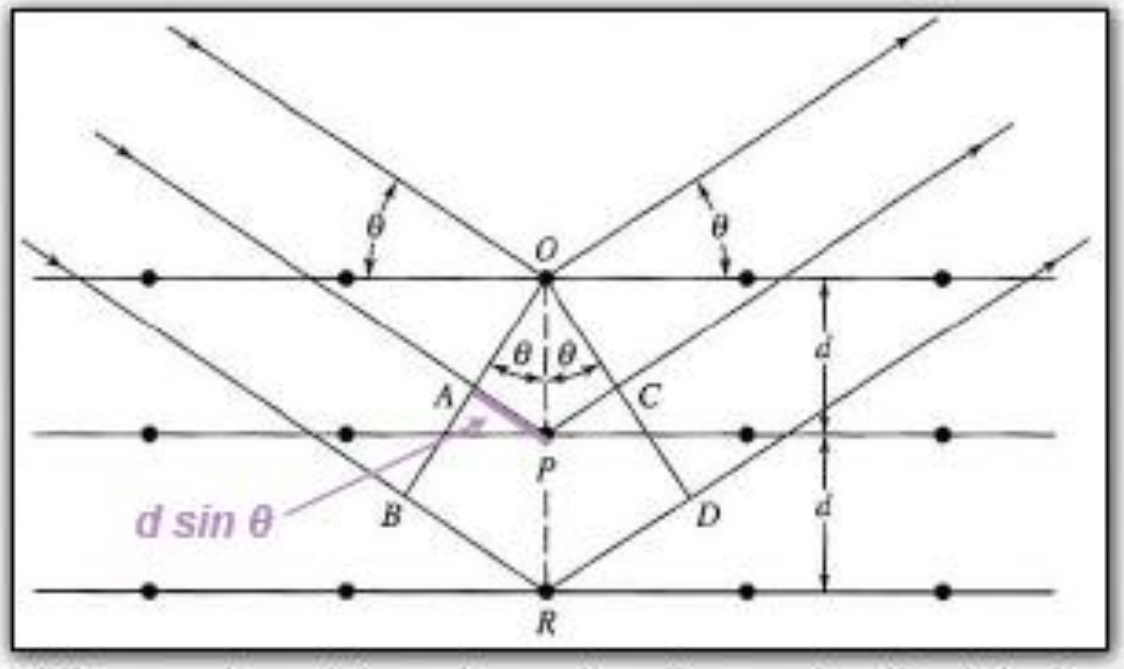
Matrix effects make this difficult as a quantitative measure. Careful work makes it viable in specific situations (sulfur impurities in hydrocarbon fuels).

X-Ray Fluorescence

- the practical way of quantitation with x-rays.
- just use an excitation source that exceeds the absorption edge for the analyte, and monitor the fluorescence at that wavelength.
- excitation can come from any source.
- very common to be excited by electron beam in SEM. Use for atomic identification, atomic mapping of surfaces. (See EDX).

X-Ray Diffraction

Perhaps most common scientific use of x-rays (beyond medical imaging). X-rays scattered from planes of atoms.

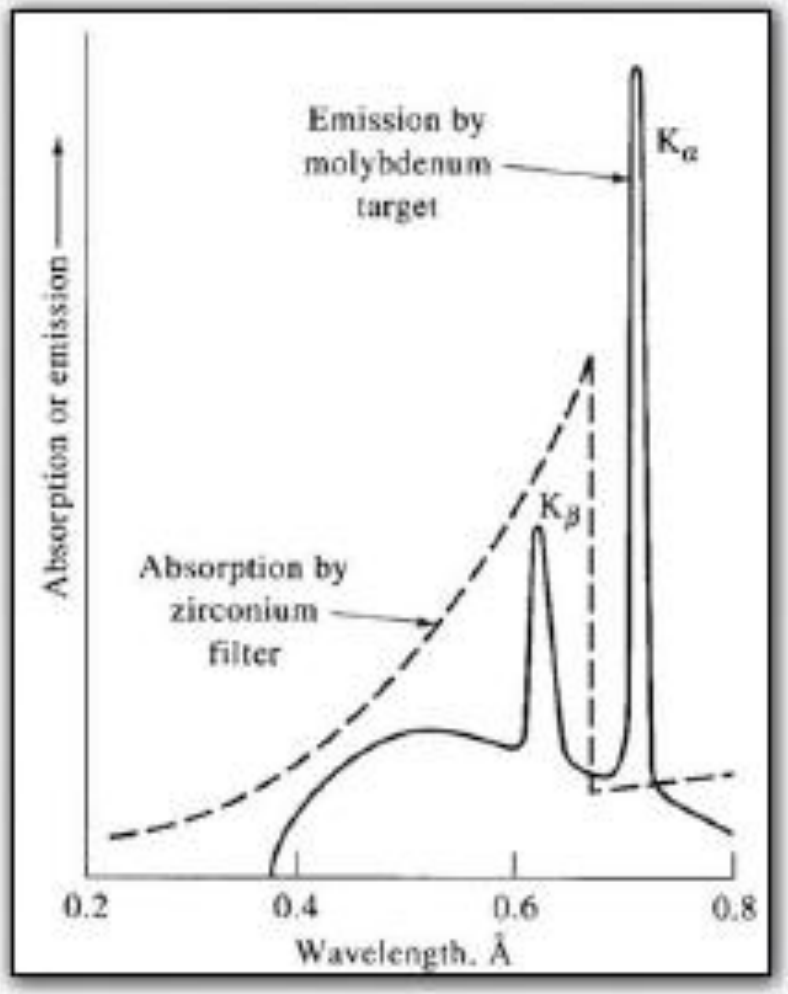


When path difference is an integral wavelength, constructive interference occurs.

$$n\lambda = 2d \sin\theta$$

λ Selection - Filters

The selection of certain materials can be used to narrow the emission of an x-ray source by filtering. Here is an example of using a Zr filter to remove the K_b and much of the Bremsstrahlung radiation from a Mo target.

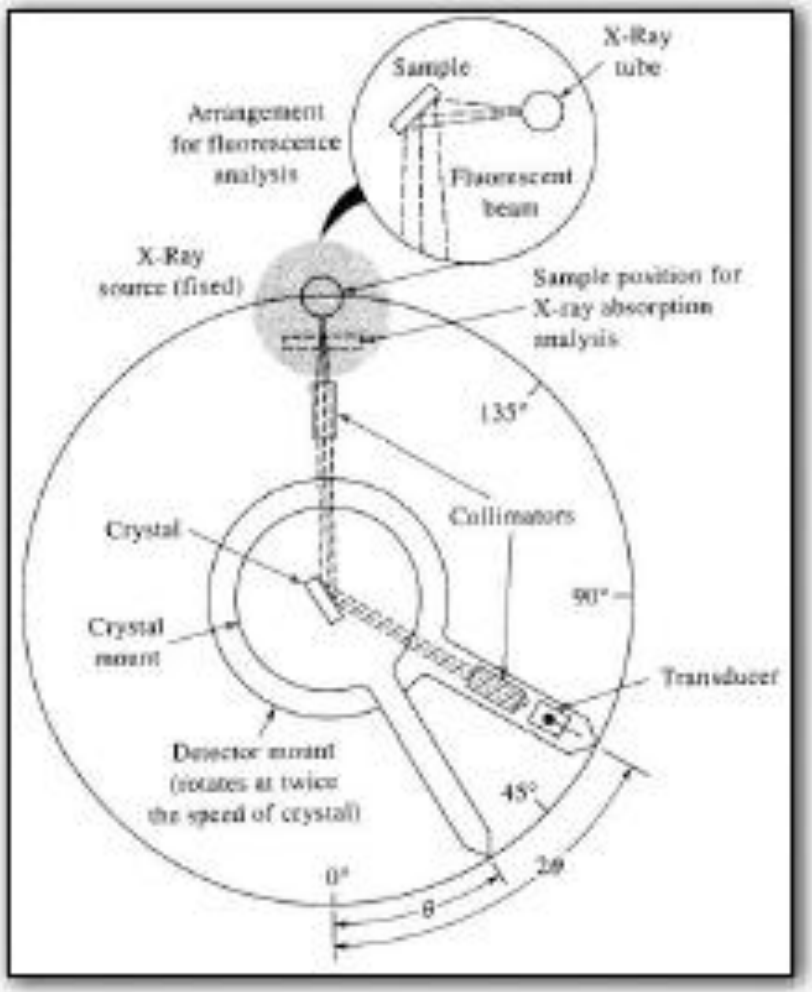


λ Selection - Monochromators

As with longer wavelength light, we can use a diffraction grating to disperse the radiation. However, the wavelengths are such that we must use a crystal as the grating.

Turn crystal an angle of θ; move detector a distance of 2θ.

Crystal with large spacings, can cover a large range of wavelengths, but has a smaller dispersion. Differentiate Bragg equation to see that dispersion is inversely proportional to d and to the cosine of the angle.



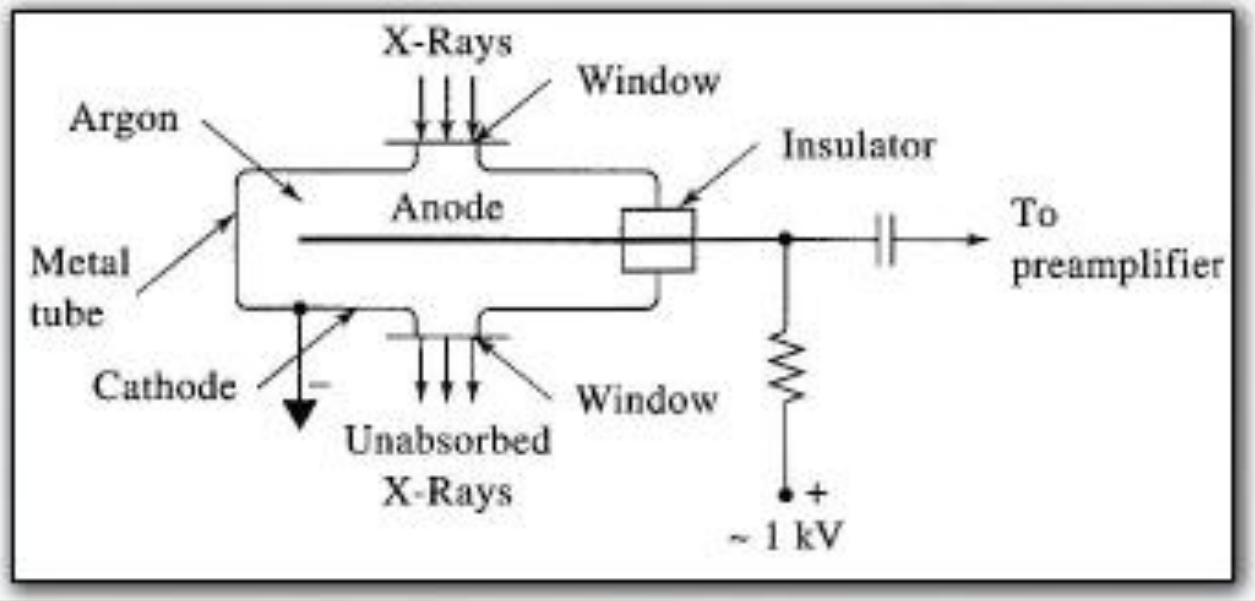
Transducers

How do you detect an x-ray photon? In the old days you could use photographic paper. Improved convenience, speed, and reproducibility comes with electronic transducers. There are three main types:

- Gas Filled (different operating conditions lead to three distinct types).
  - Ionization Chamber
  - Proportional Counter
  - Geiger Counter
- Scintillation Counter
- Semiconductor Transducer

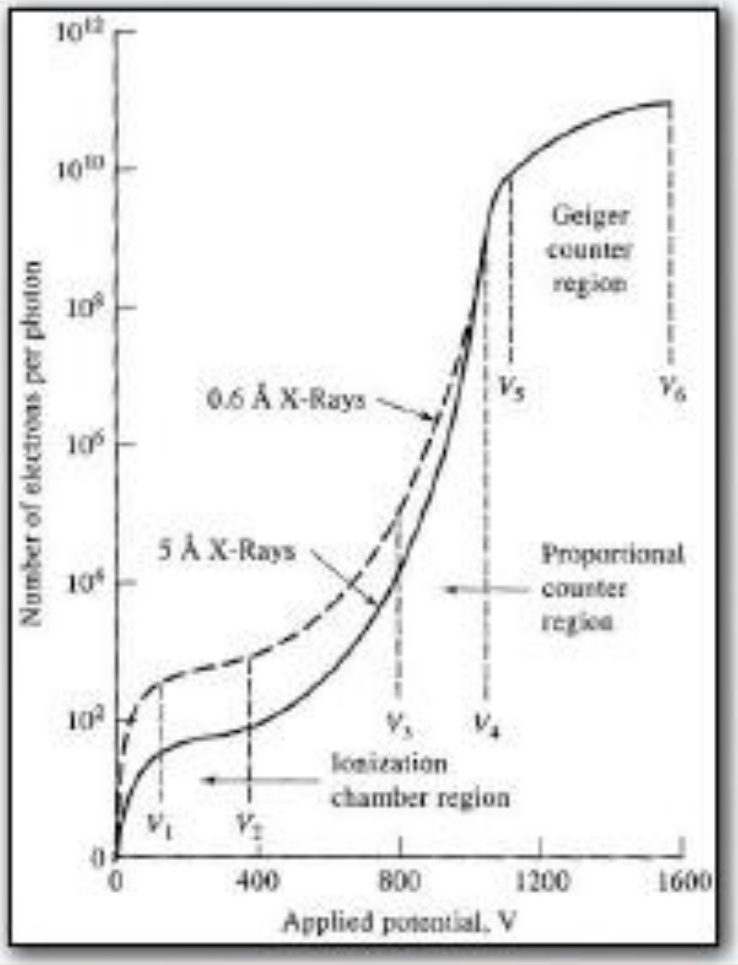
Gas Filled Design

Fill a tube with a gas such as Ar. X-rays enter through a window (Be or Mylar). (Why Be?)
Each photon ionizes an Ar atom, ejecting a photoelectron. Photoelectron ionizes other gas atoms, producing more free electrons. Electrons are attracted towards an anode. Cations attracted towards surrounding cathode wall. Measure current flow to ground. Magnitude of current depends upon bias voltage.



Gas Filled Response

Different bias potential produces a different response. Three distinct ranges give rise to three different instruments.



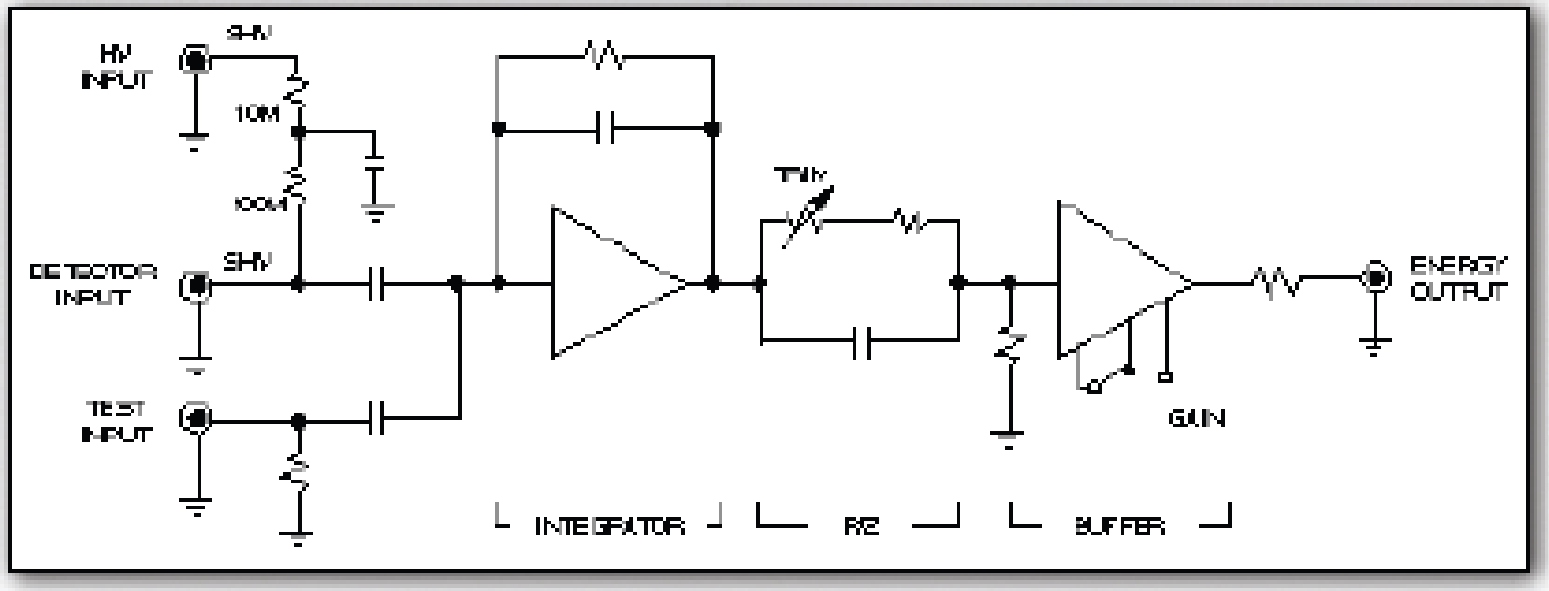
Geiger Counter

Use a high bias voltage. Count events. Will detect all kinds of high energy processes, including x-rays. Large gain so very sensitive, but response is not linear, so no energy analysis possible. Count events to determining intensity of source.

This small unit can count up to 50,000 cps.

Proportional Counter

Now the size of the pulse matters. A higher energy photon produces a linearly greater number of electrons. Measure the size of the pulse and relate this to the analyte's activity. Below is a schematic of a pre-amplifier used by Canberra as a proportional counter. Note that it has an integrator to measure the magnitude of the pulse.



Ionization Chamber

Bias voltage is very small and gain is correspondingly small. Currents that reach the anode are in the femtoamp to 10's of attoamp range.

Have been used in radiochemical measurements (probing α and β and γ decay processes).

More common to find proportional counters now.

Ionization detectors sold by Toshiba.

Photon Counting

Usually we relate a measured current to the magnitude of a response at a transducer. When the occurrence of an event is comparatively rare, the current consists of small bursts of electron flow. The current is an average over time of this sporadic flow. Size of bunches may be significant. If not, then just count the number of bunches and related this to the transducer response.

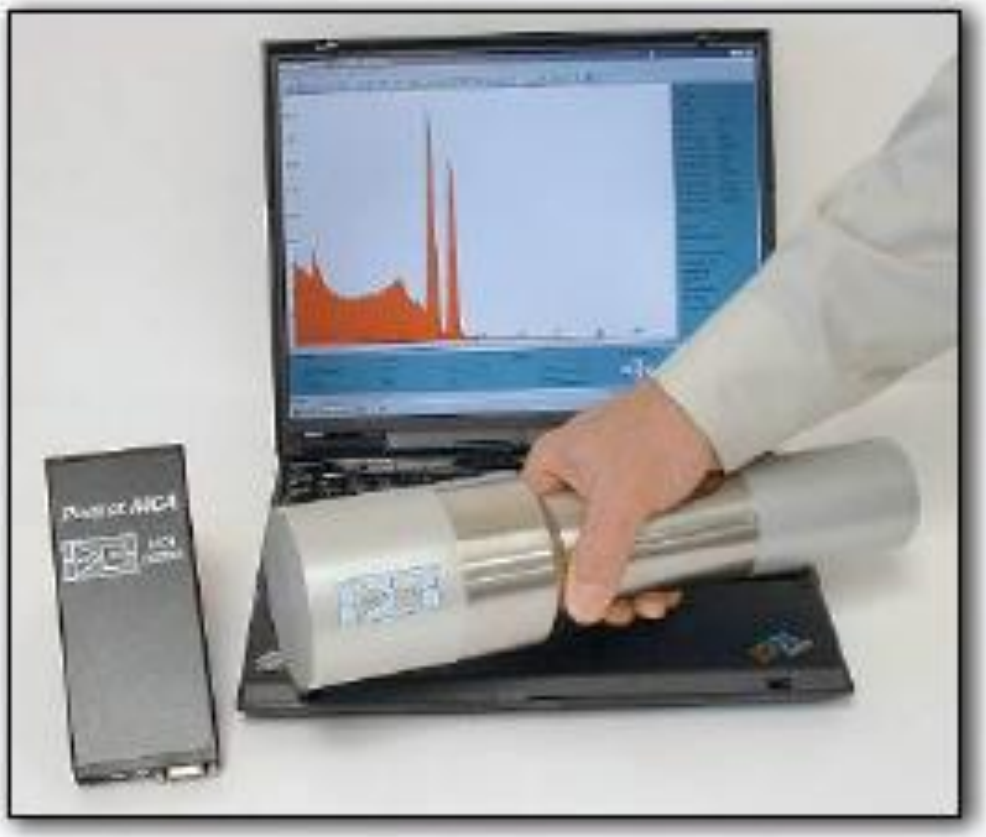
Use a pulse height analyzer (hi-lo discriminator). Pulses too small are ignored as coming from noise. Pulses too large are ignored as false readings (perhaps from a cosmic ray). Everything in between, no matter if it is near the bottom or the top in magnitude, is counted as a single event.

When the count rate increases to point that exceeds response of instrument, then a constant current starts to develop. Return to current measurement technique.

Scintillation Counter

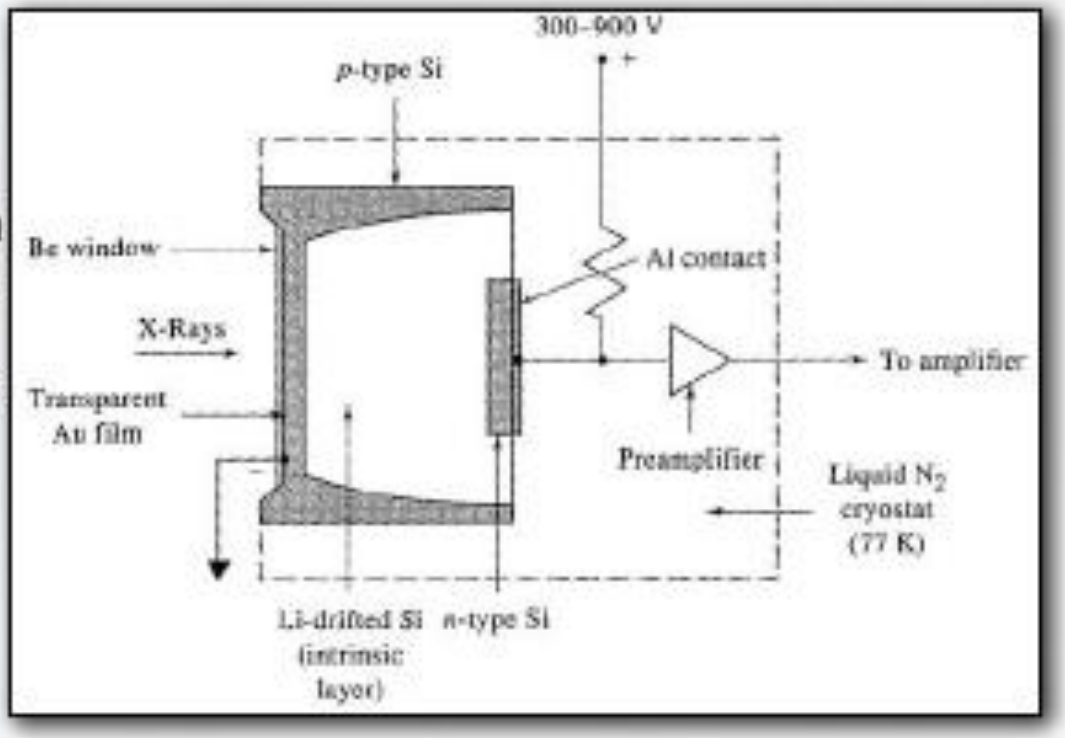
Use a phosphor screen. Place a PMT close by to count the flashes of light.

Modern device uses crystal of NaI, doped with Tl (0.2%). Many photons ejected. Number of induced flashes is proportional to the x-ray photon energy. Hence, is also a proportional counter using pulse height analysis. New crystals using various organic scintillators are being developed for improved performance.

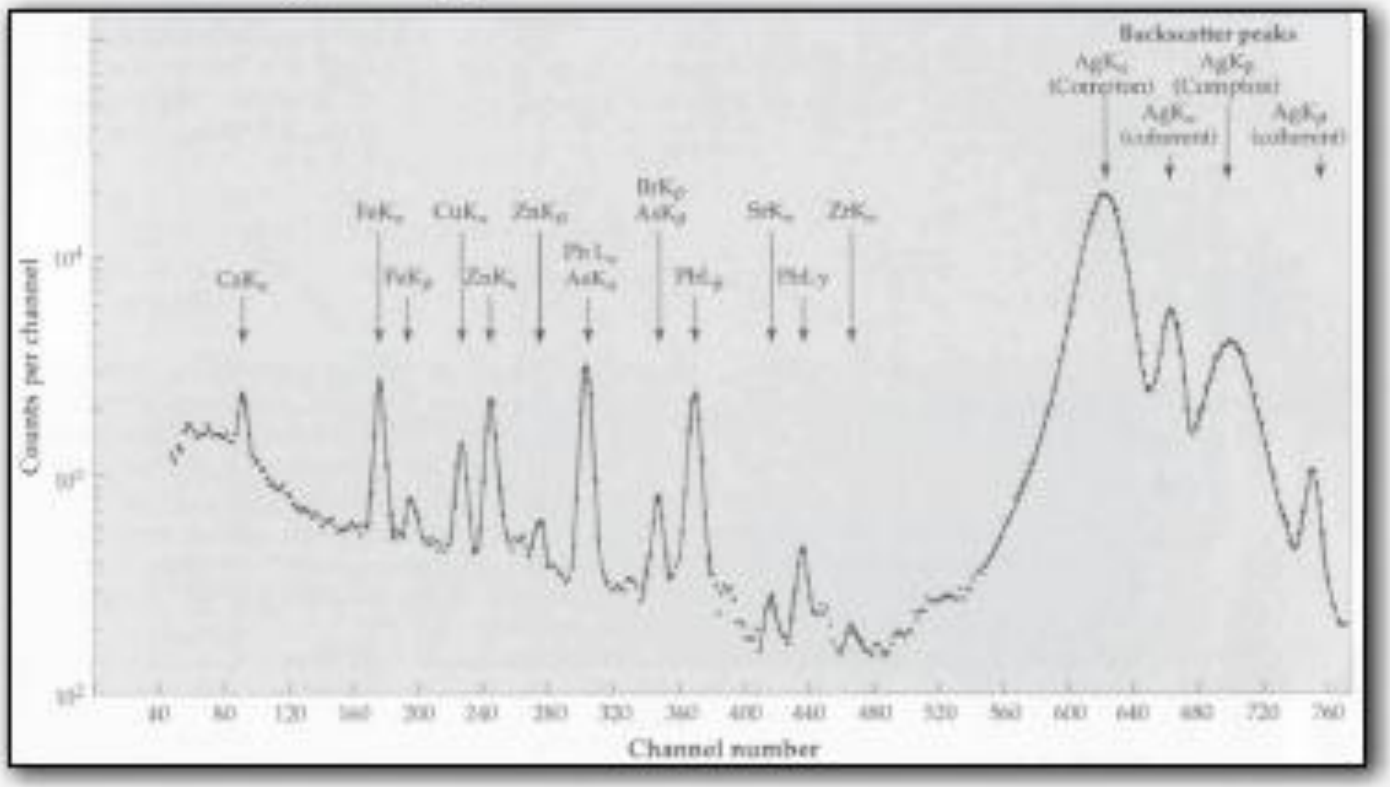


Semiconductor Transducer

The most modern detector is a solid state device that behaves much like the proportional counter. Here a Si structure with n and p doped regions has Li embedded in a central intrinsic Si region. An x-ray photon, produces a very high energy photoelectron, which in turn produces thousands of secondary electrons. This increases the conductivity between the two terminals and a pulse is measured. The pulse is proportional to the energy of the x-ray.



X-Ray Spectrum



Numerous elements. Broad peaks are a result of elastic and inelastic scattering in the sample.

Instruments

- **Non-Dispersive**

  Dedicated to a very specific task, using filters to sort out the signal.

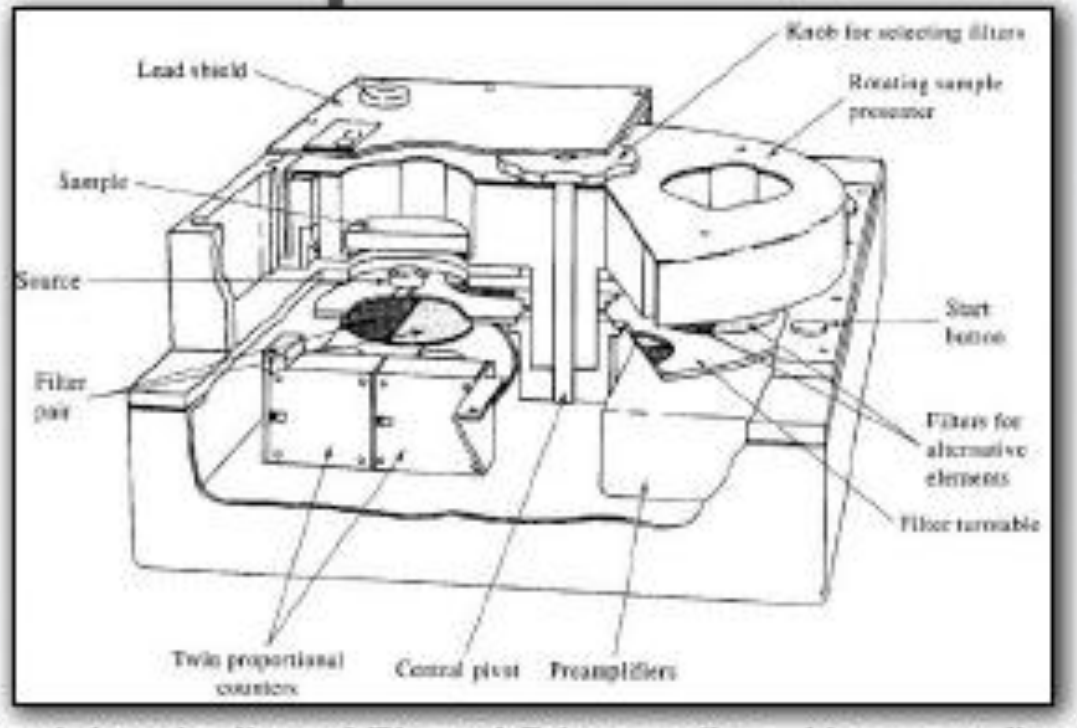
- **WDX (Wavelength Dispersive X-ray)**

  Much like a spectrometer in other regions of the spectrum, it disperses the light with a grating and detects a selected band.

- **EDX (Energy Dispersive X-ray)**

  Directly measures the difference in energy of the x-rays and measures the signal without spatially dispersing the wavelengths of the x-rays.

Non-Dispersive



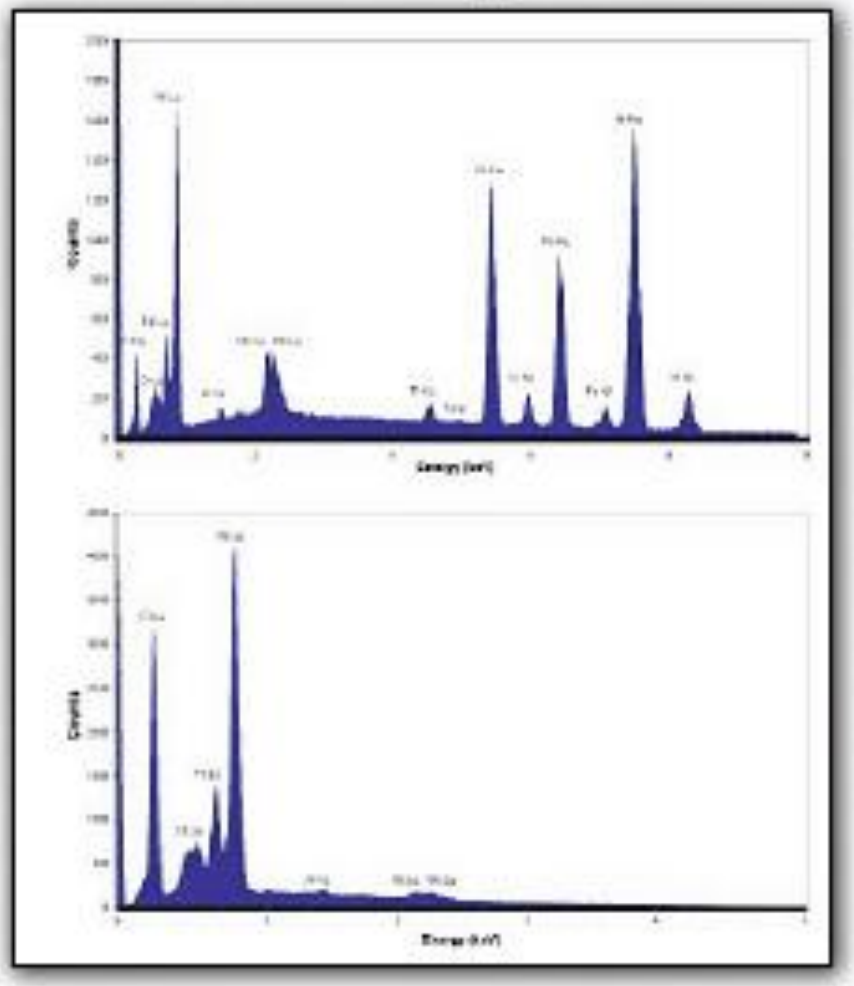
Used for the determination of Pb and S in gasoline. Uses a radioactive source (iron-55); irradiates sample and any sulphur fluoresces with a photon at 5.4 Å. Two filters – one just below the S line and the other just above – lead to two detectors. The difference between the two is the S signal. Analysis for S takes about 1 min.

EDX

Energy Dispersive X-ray Spectrometry (also called EDS) uses a solid state detector, cooled to LN_2 temperatures, to energy analyze the x-ray source.

Its strength is its speed and convenience. Is often added to an SEM, using the SEM electron beam as an excitation source. X-ray analysis provides elemental information, which can be correlated to the topography of the SEM image.

EDX Spectra



Here are the spectra from a Ni alloy. The top is excited with an electron beam operating at 20 kV. It excites the K lines of the elements and one can easily separate Cr, Fe, and Ni for confident analysis. The lower spectrum is taken at 5 kV where only the L transitions are available. A better instrument is needed to separate the various elemental lines. Low beam energy is desirable to avoid scattering outside the initial excitation zone and degrading the spatial resolution. Balance is required.

WDX

Wavelength dispersive instruments were largely replaced by EDX because of the ease of use. Recent developments in automation of changing crystals and alignment, have brought a resurgence in their use. They have a much better resolution than EDX, but require several crystals to act as gratings to cover the entire spectrum. It uses gas filled proportional counters as detectors.

WDX Diffraction Crystals

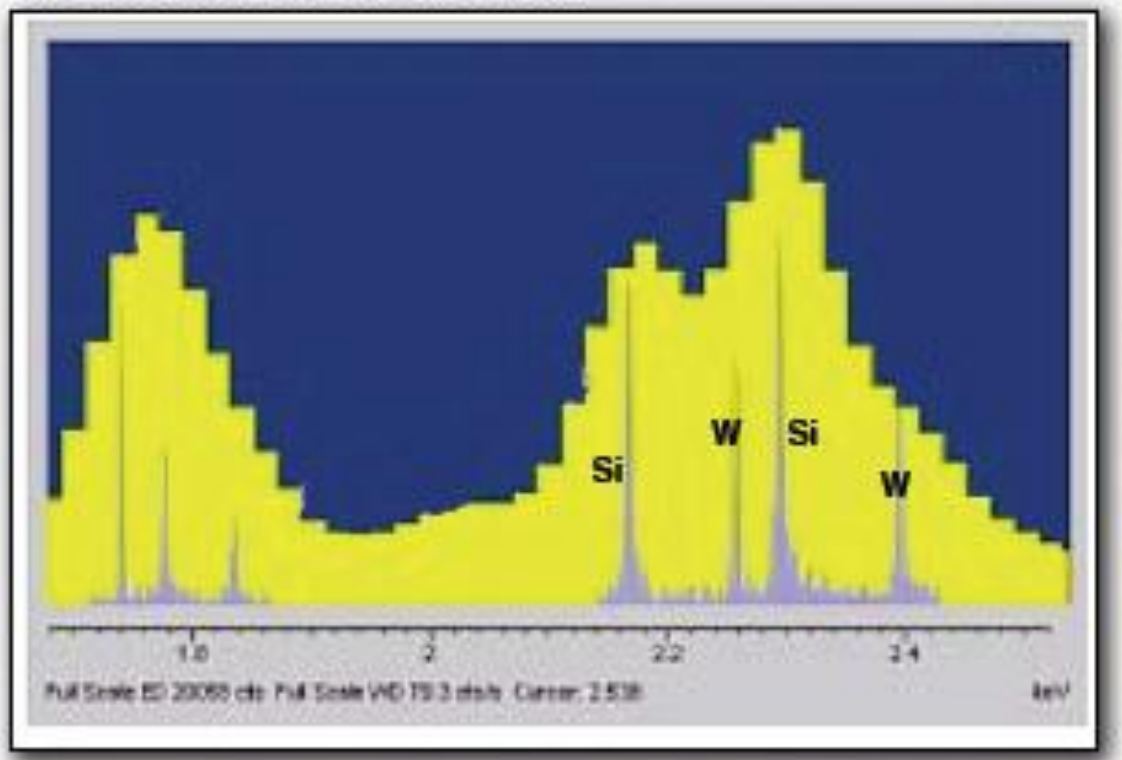
To achieve good diffraction over the entire range of atomic x-ray wavelengths, several crystals are needed. Switching between crystals and maintaining alignment automatically is the key to making WDX a useful technique.

These crystals have the specified d spacing and can cover the K_a lines of the specified elements. LSM is "layered synthetic microstructure".

LiF(220)	1.42365 Å	V to Y
LiF (200)	2.01334 Å	Ca to Ge
Pentaerythritol	4.37 Å	Si to Ti
Thallium acid phthalate	12.875 Å	O to Si
LSM-060 (W-Si)	30.5 Å	C to F
LSM-080 (Ni-C)	39 Å	B to C
LSM-200 (Mo-B_4C)	102 Å	Be and B

WDX Spectra

The yellow spectrum is an EDX spectrum of a sample of Si. The 2 prominent peaks are Si K_a. The sharper WDX spectrum is superimposed on the yellow. Here the presence of W was masked by the Si in the EDX spectrum but is clearly observable in the WDX spectrum.

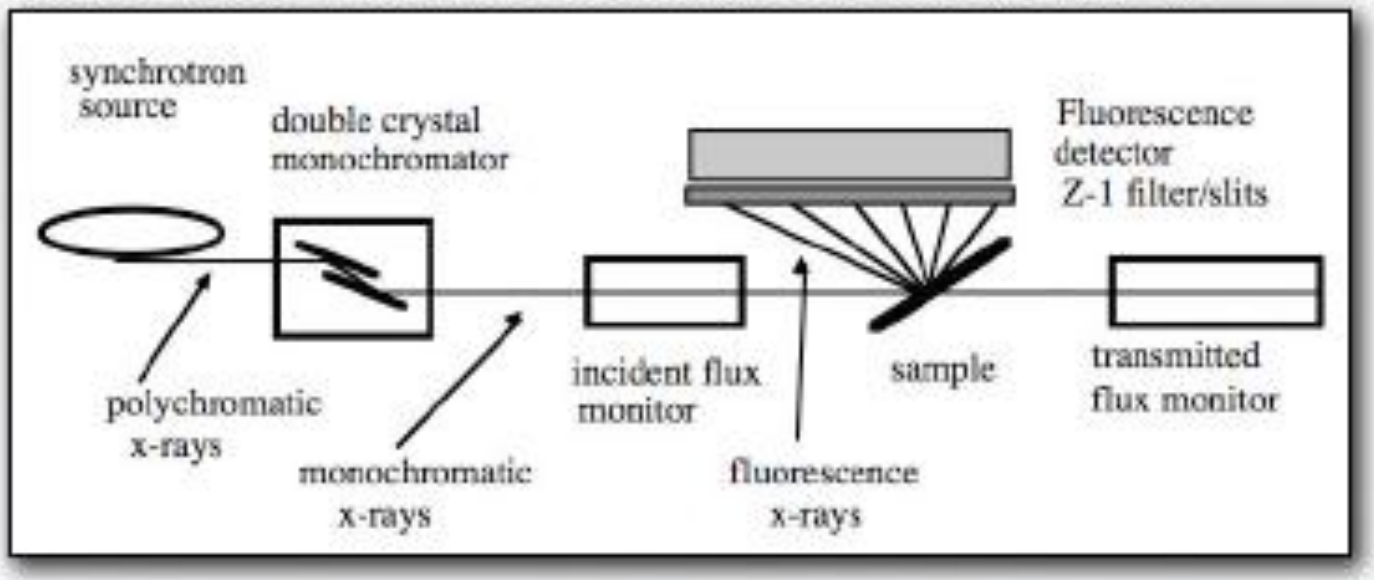


EDX is used for rapid, routine analysis and WDX is called in for more careful analysis. WDX also has a greater dynamic range.

X-Ray Absorption

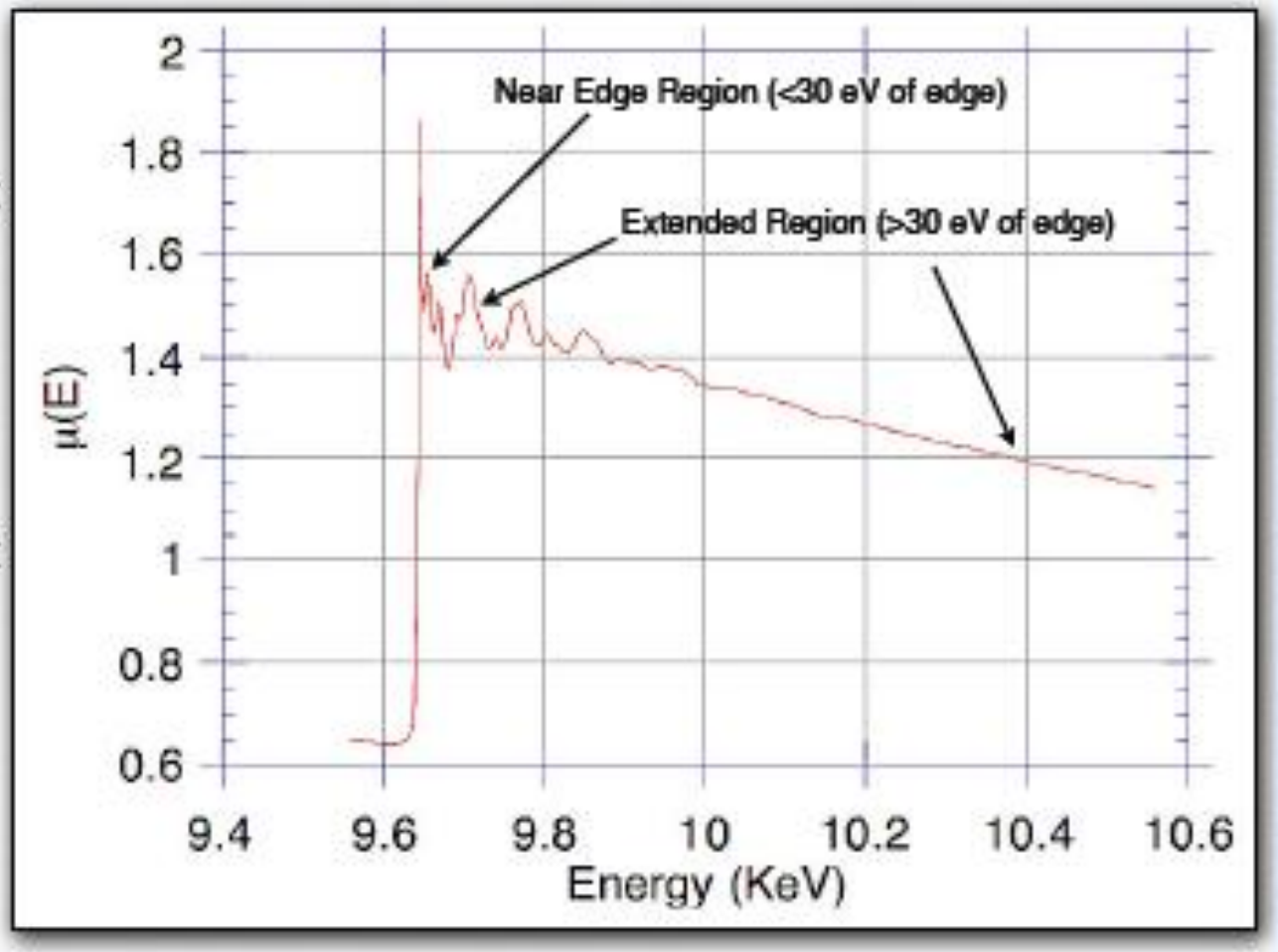
Marginally useful quantitative tool. Large matrix effects. Single heavy element dispersed in matrix of light elements.
However, important qualitative tool in surface structural analysis

- Extended X-ray Absorption Fine Structure (EXAFS).
- Near-Edge X-ray Absorption Fine Structure (NEXAFS) also called X-ray Absorption Near-Edge Structure (XANES).
- Surface Extended X-ray Absorption Fine Structure (SEXAFS).

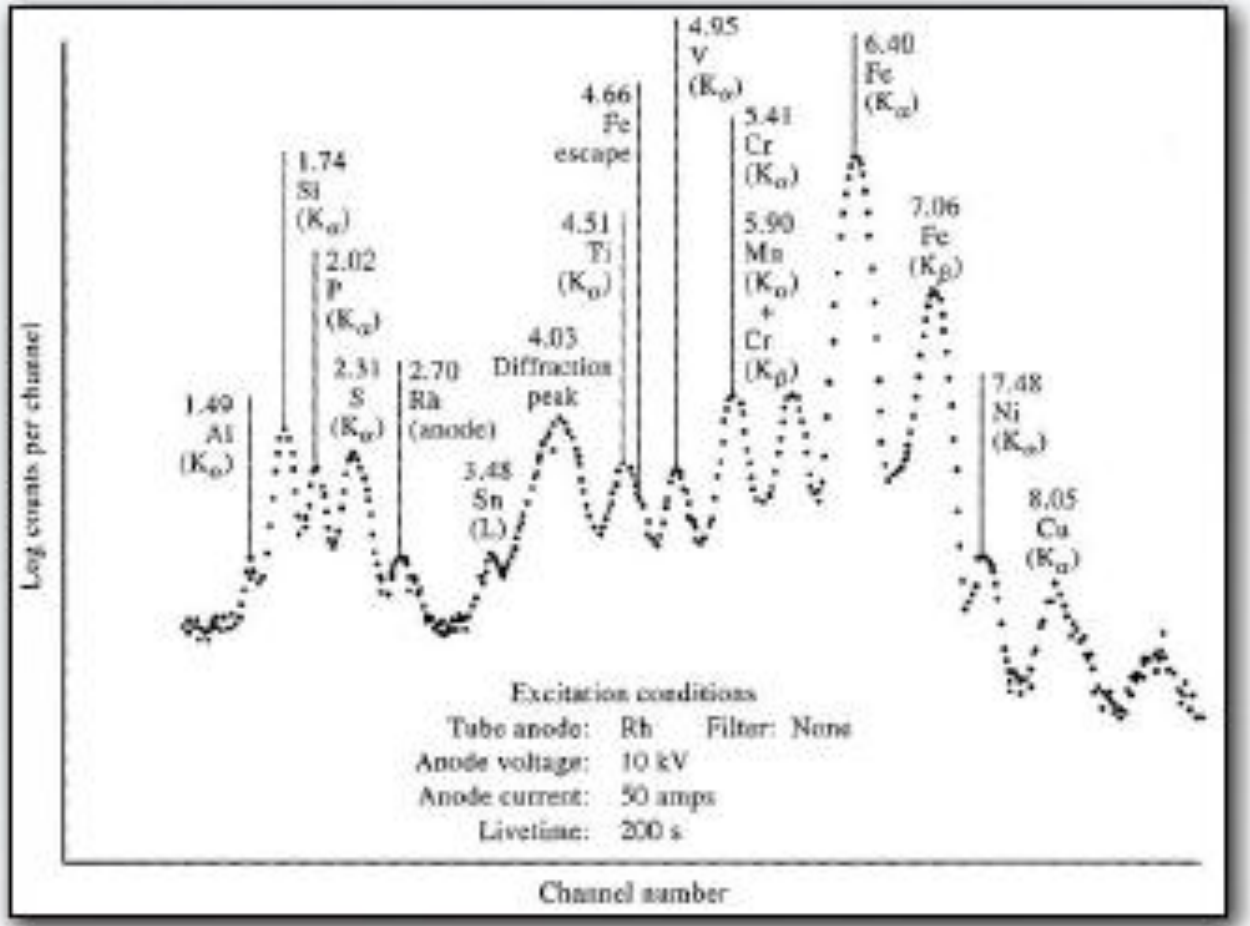


XAFS Spectra

Near-Edge, transitions to bound states. Information about local site symmetry, oxidation state. Extended, transitions to continuum. Information about local bond distances.



X-Ray Fluorescence

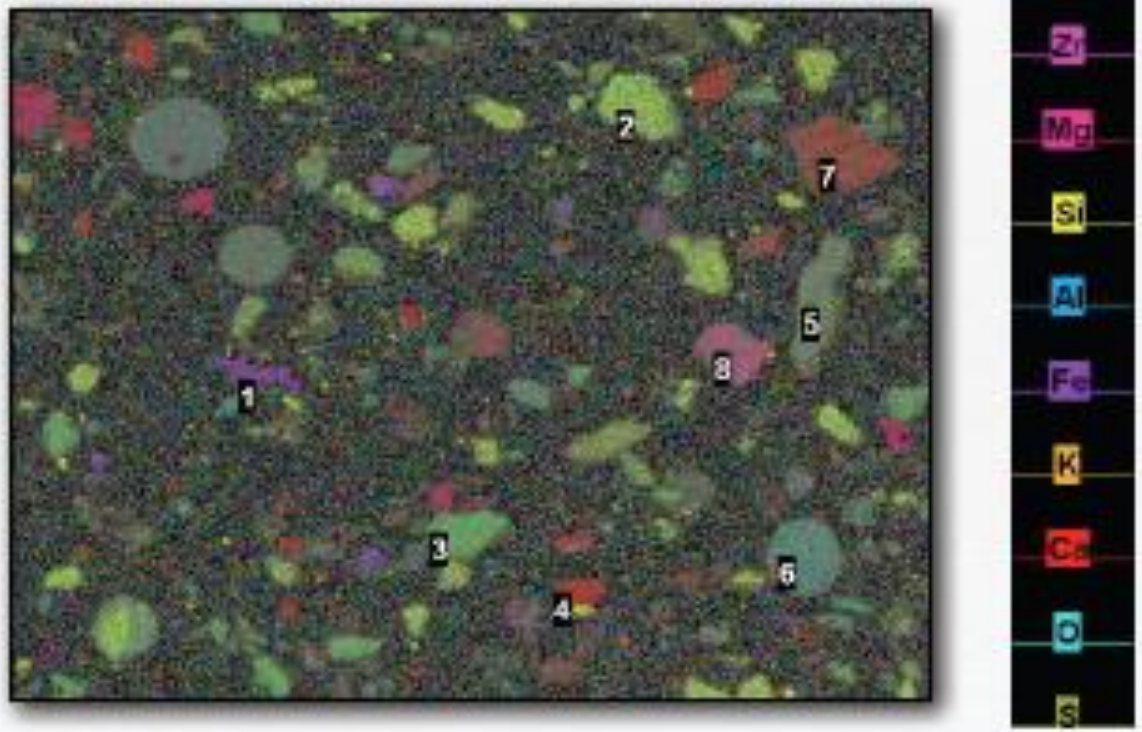


The spectrometers mentioned earlier can be used to monitor the fluorescence arising from a sample which has been irradiated with x-rays from another source. This readily gives good qualitative information and with careful calibration and matrix control can give good quantitative information.

E-Beam Stimulated Fluorescence

Here the electron beam in a scanning electron microscope (SEM) is used to excite a sample with spatial resolution of the beam spot size. Monitoring x-ray fluorescence for several atomic transitions can map the relative concentration of the atomic species and create a chemical map of the surface.

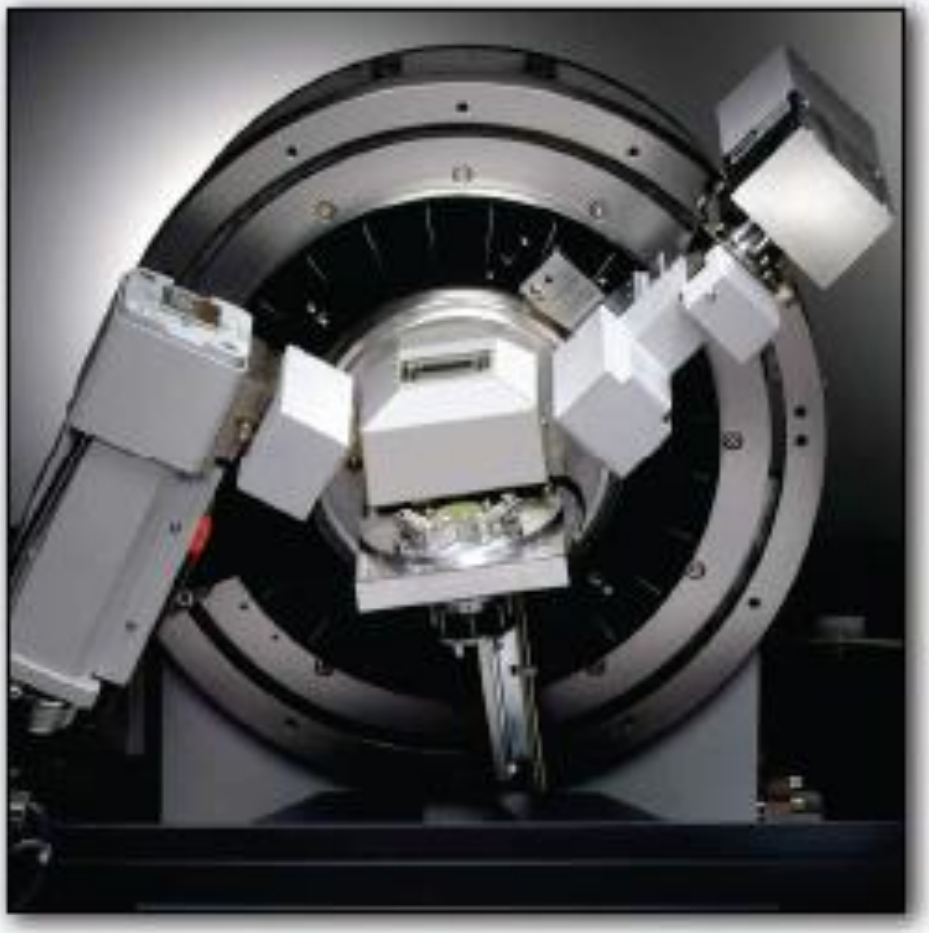
An analysis of a collection of dust particles from Beijing, done at Surface Science Western, identifying the various elemental entities.



Diffraction - Single Crystal

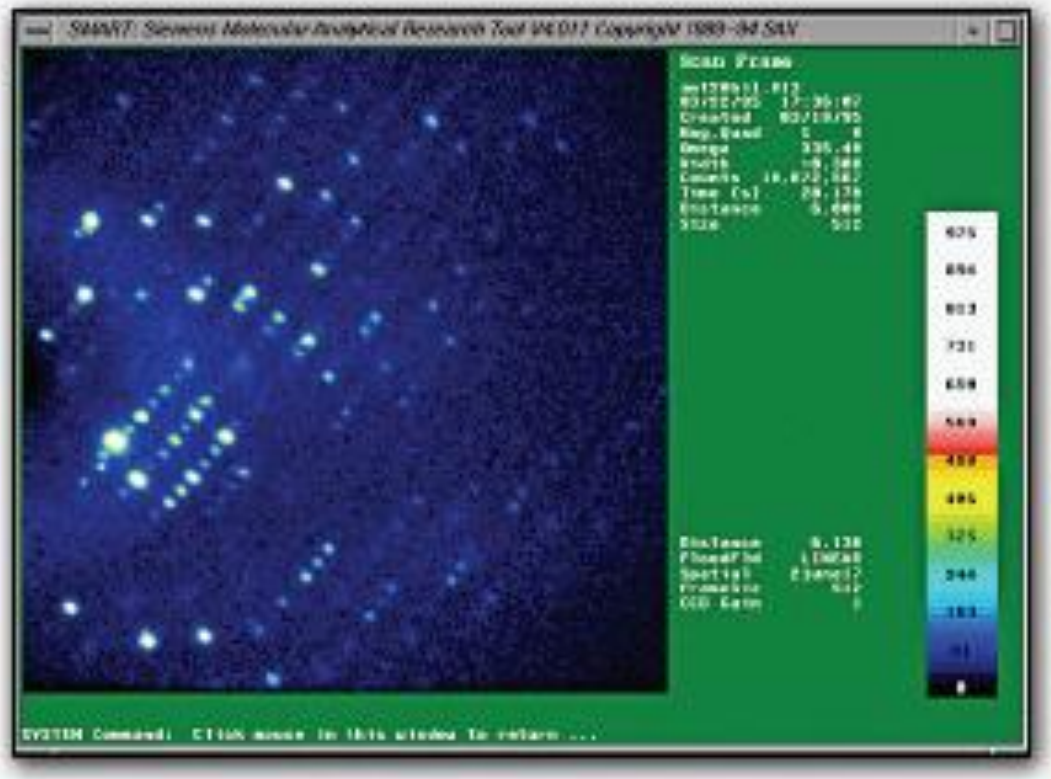
Grow single crystal sample.

Goniometer can move sample and detector freely through all angles to measure diffracted beam intensity.



Single Crystal Pattern

Take a single crystal, move an area detector throughout the space around it, and collect x-ray vs. position information. Very heavy data processing can work out the arrangements of the atoms in the crystal. Becoming critically important for solving large molecule structure problems. Takes 6 hours to acquire sufficient data to start the data analysis.



Diffraction - Powder

In this case, the sample is not single crystalline, but rather is a powder. The grains that make up the powder are individually crystalline, but they are mixed together randomly. Diffraction spots in the single crystal case, become rings from all possible orientations of crystallites in the sample. The angle to the ring is unique for each crystal plane and the angle 2θ is the measure to determine this. Because diffraction pattern is symmetric, detector only needs to move along one line through the plane to acquire the powder pattern spectrum. Faster data acquisition, less sample preparation, get all information about d spacings. No information about internal structure of unit cell.

Powder Pattern Spectrum

A series of powder XRD. Sample is urinary tract antibacterial drug nitrofurantoin monohydrate. Spectra were taken at increasing temperatures, between 90 °C and 150 °C. At around 125 °C, a phase transformation occurs where it dehydrates. This affects its bioavailability and drug effectiveness.