

### 3<sup>rd</sup> year XRF Spectroscopy

- Dr. Alan Ryder (R222, Physical Chemistry)
- 2 lectures: 1 exam question.
- Notes on:  
[www.nuigalway.ie/nanoscale/3rdspectroscopy.html](http://www.nuigalway.ie/nanoscale/3rdspectroscopy.html)
- “Analytical Chemistry”, Kellner/Mermet/Otto/etc.
  - Chapter 24.4 (p. 668-695). 4 copies in library.
- X-Ray fluorescence spectroscopy 2<sup>nd</sup> ed., R. Jenkins: Wiley.

1

### XRF Resources: internet

- Micro- and Trace Analysis Centre (MiTAC) at the University of Antwerp (UA) , the ChemometriX group:
  - <http://www.chemometrix.ua.ac.be/xrftrain/>
- Manufacturer websites (*good for applications etc.*):
  - [www.bruker-axs.de/fileadmin/user\\_upload/xrfintro/index.html](http://www.bruker-axs.de/fileadmin/user_upload/xrfintro/index.html)
  - [www.amptek.com/xrf.html](http://www.amptek.com/xrf.html)
  - [www.horiba.com/scientific/products/x-ray-fluorescence-analysis/](http://www.horiba.com/scientific/products/x-ray-fluorescence-analysis/)
  - [www.rigaku.com/xrf/](http://www.rigaku.com/xrf/)
- Journal:
  - X-Ray Spectrometry, Wiley Interscience.

2

### XRF spectroscopy: 4 topics

- Theory:
  - Interaction of X-rays with matter
- Instrumentation:
  - Sources, detectors
  - Energy and Wavelength dispersive instruments
- Sampling & Standards:
  - Solids & liquids.
- Matrix effects:
  - Mass absorption, secondary enhancement

3

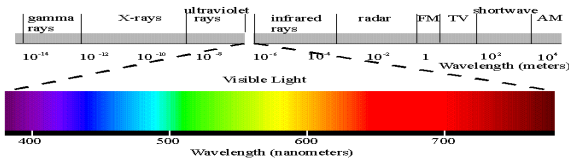
### 3<sup>rd</sup> year spectroscopy: 1<sup>st</sup> Topic

- General Features of X-Ray Fluorescence Spectroscopy:
  - Energies involved
  - Types of emission.
  - Brehmstahlung, Auger, Compton, Rayleigh
- Be able to show an understanding of the theories behind XRF and explain all the terms.

4

## The Electromagnetic Spectrum

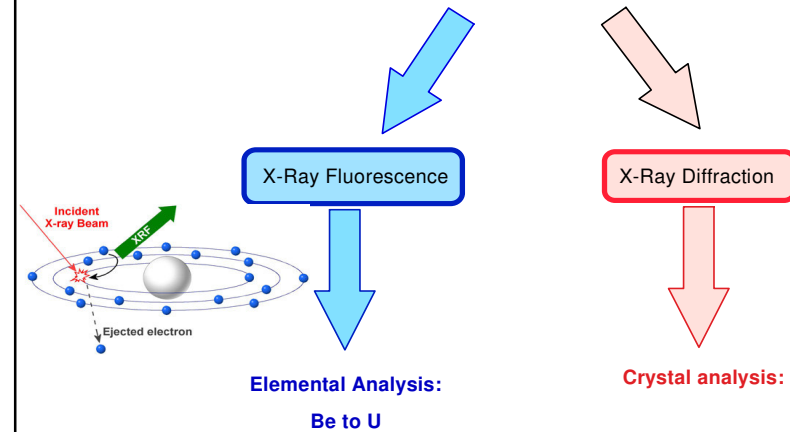
Region	Frequency $s^{-1}$	Wavelength
Radio F	$10^6$ — $10^8$	300—3 m
Micro Wave	$10^{10}$ — $10^{12}$	30—0.3 mm
IR	$10^{12}$ — $10^{14}$	300—1 $\mu$ m
UV-VIS	$10^{14}$ — $10^{16}$	1000—30 nm
X-RAY	$10^{16}$ — $10^{19}$	100—30 pm
$\gamma$ -RAY	$10^{19}$ — $10^{22}$	30—0.03 pm



[Table of Contents](#) [Visual Stimulus](#)

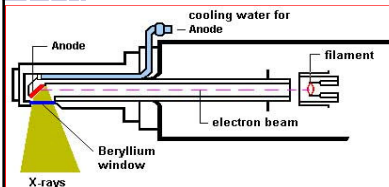
5

## X-Ray Methods of Analysis



6

## X-Ray sources I



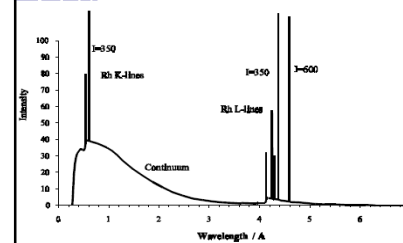
- Electric current through a filament, which causes electrons to be emitted.
- Electrons are then accelerated by high voltage (typically 20 and 100kV) towards an anode (target).
- A thin beryllium window is used to allow the X-Rays out of the generator, and onto the sample.
- Needs high voltages/cooling water etc. Only ~1-2%, of energy is radiated in the form of X-rays.

When electrons impact the anode material, two processes dominate:

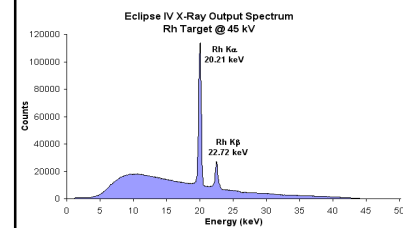
- Deceleration of the electrons when they hit the anode causes a broad X-Ray continuum to be emitted: *bremstrahlung* (German: braking radiation).
- A fraction of the electrons will cause characteristic X-Ray fluorescence (sharp lines) from the anode material (e.g. Tungsten, rhodium, molybdenum).
- Different anode materials give different wavelengths of X-Rays

7

## X-Ray sources II



Many spectrometer manufacturers use rhodium (Rh) as a standard anode material because the characteristic energies of this element are simultaneously suitable for exciting both heavy and light elements.



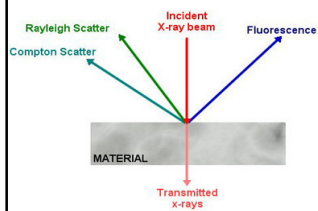
Line	Energy	Wavelength	Heaviest Element
Rh $K\alpha_1$	20.214 keV	0.0613 nm	Molybdenum (Mo)
Rh $K\alpha_2$	20.072 keV	0.0617 nm	Molybdenum (Mo)
Rh $K\beta$	22.721 keV	0.0546 nm	Ruthenium (Ru)
Rh $L\alpha_{1,2}$	2.694 keV	0.4601 nm	Sulphur (S)
Rh $L\alpha_2$	2.834 keV	0.4374 nm	Chlorine (Cl)

Eclipse-IV (Oxford Instruments) output spectrum at 45 kV.

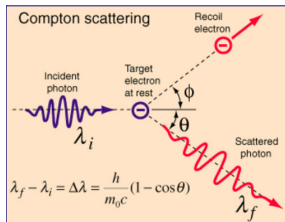
<http://www.bruker-axs.de>

8

## Interaction of X-rays with matter



- **Rayleigh scattering: elastic scattering**  
X-Ray photons from the tube change their direction in the sample material without losing energy and can thus enter the detector and be measured:
  - The peaks of the anode material (e.g. rhodium) appear in XRF spectrum. If the element rhodium in the sample material is to be analysed using an Rh tube then the characteristic radiation coming from the tube must be absorbed by a primary beam filter before it reaches the sample.

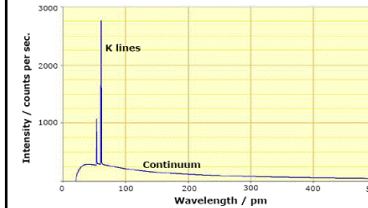


- **Compton scattering: inelastic scattering**  
The X-ray photons strike the sample elements' electrons, exchange of energy. X-Ray quanta lose energy:
  - a somewhat wider peak appears on the low-energy side of the appropriate Rh peak. These peaks are called "Compton peaks."

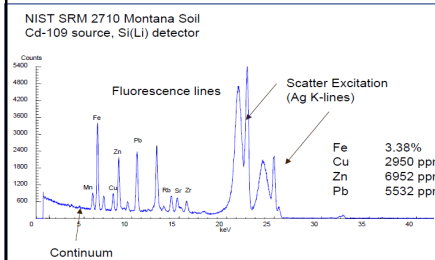
<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/compton.html>

9

## Characteristics of emission



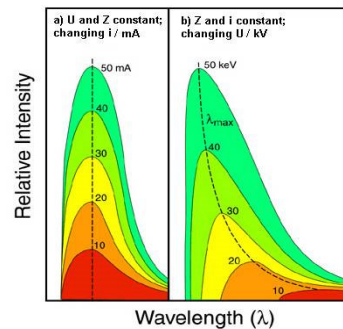
- X-Ray spectra (from tubes or samples) have two features:
  - A weak, broad continuum
  - Sharp superimposed lines.



10

## Bremsstrahlung I

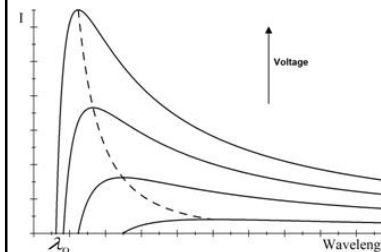
- German for: *Braking Radiation*
- X ray radiation emitted by charged particles, such as electrons, which are braking around other charged particles, such as an atom nucleus.
- It forms the continuum component of the x-ray spectrum generated by an x-ray tube.



<http://www.nt.ntnu.no/users/floban/KJ%20%203055/X%20%20Ray/Bremsstrahlung.htm>

11

## Bremsstrahlung II



$$\lambda_0 = \frac{hc}{U}, \quad I_M = k_2 i Z U^2$$

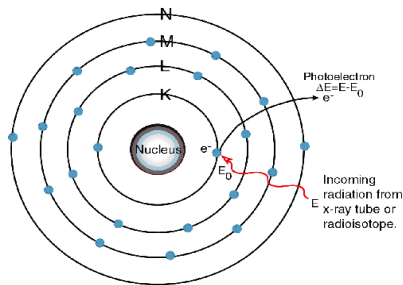
$U$  = tube voltage,  $i$  = tube current,  
 $k$  = an empirical constant.

$\lambda_0$  = minimum wavelength.

- Related to the atomic mass ( $Z$ ):
- Nearly always present in XRF spectra.
- Kramer's formula:
  - an approximation of the spectral distribution. Its derivation ignores the self-absorption of x-rays & electron backscattering effects.

12

## XRF: STEP 1 Photoelectron Emission



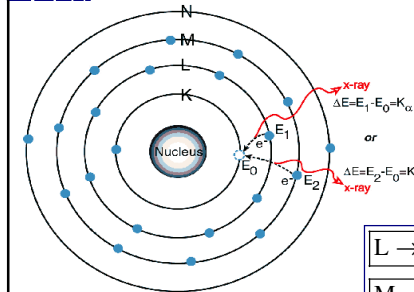
- Primary X-Ray ejects inner shell electron:
- X-Ray has to have sufficient energy,  $>$  binding energy of the electron.

$$E_{pe} = E_{XRay} - E_0$$

$$E_0 > E_1 > E_2 > E_3 \text{ etc.}$$

13

## XRF: K Line emission



- Vacancy in inner K shell.
- Electron drops in from outer L/M/N shells.
- Excess energy emitted as an X-Ray.

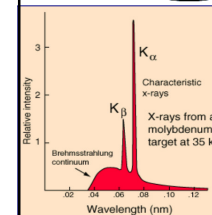
$$L \rightarrow K \text{ transition: } K_{\alpha} \text{ line: } \Delta E = E_1 - E_0$$

$$M \rightarrow K \text{ transition: } K_{\beta} \text{ line: } \Delta E = E_2 - E_0$$

$$N \rightarrow K \text{ transition: } K_{\gamma} \text{ line: } \Delta E = E_3 - E_0$$

Generally  $K_{\alpha}$  line is more intense than  $K_{\beta}$

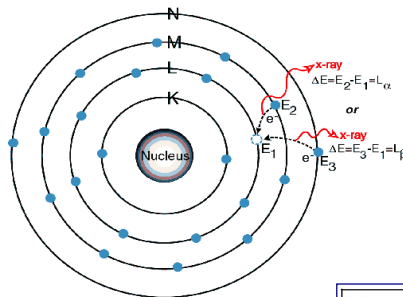
Photon energies:  $K_{\gamma} > K_{\beta} > K_{\alpha}$



<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/xrayc.html#c1>

14

## XRF: L Line emission



- Vacancy in inner L shell.
- Electron drops in from outer M/N shells.
- Excess energy emitted as an X-Ray.

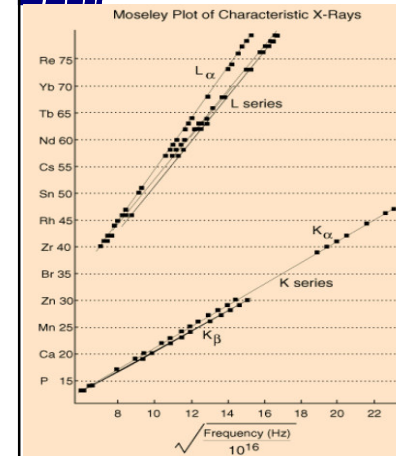
$$M \rightarrow L \text{ transition: } L_{\alpha} \text{ line: } \Delta E = E_2 - E_1$$

$$N \rightarrow L \text{ transition: } L_{\beta} \text{ line: } \Delta E = E_3 - E_1$$

Photon energies:  $L_{\beta} > L_{\alpha}$

15

## Energies of K,L lines:



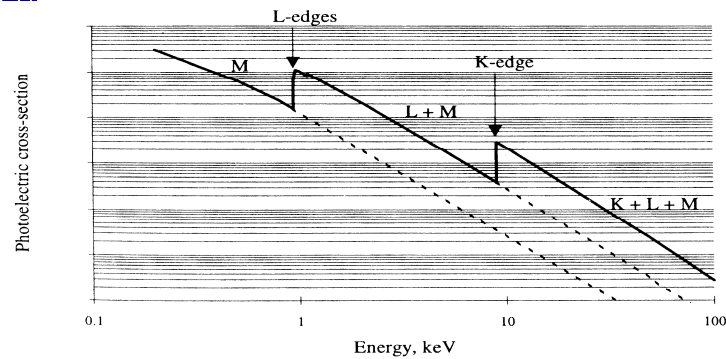
- Element dependant:
- High  $Z =$  high  $E$ , shorter wavelength X-Rays:
- When the square root of the frequencies of the characteristic x-rays from the elements is plotted against the atomic number, a straight line is obtained.

Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/moseley.html>

16

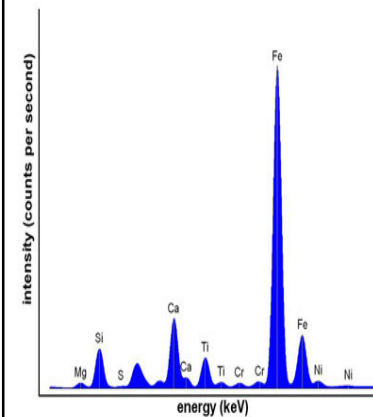
## Absorption edges



- As x-ray photon energy increases, the potential for multiple photoelectric absorption increases:
  - Edge position varies according to the element.

17

## XRF- Multiple Transitions

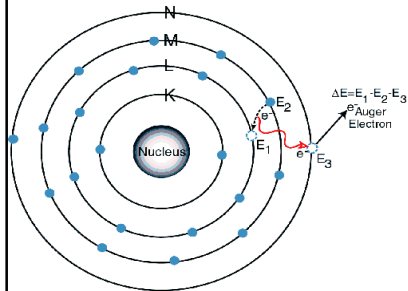


- Since most atoms comprise a number of electron orbitals (eg. K shell, L shell, M shell) a number of possible fluorescent transitions are possible.
- For example, interaction of X-Rays with an atom with K, L and M shells could result in:
  - Hole forming in the K shell: L→K & M→K,
  - Hole forming in the L shell: M→L
- Thus, for a single element, a number of XRF peaks are possible, and typically these will all be present in the spectrum, with varying intensities.
- They form a characteristic fingerprint for a specific element.**

<http://www.horiba.com/>

18

## Auger Electron Emission

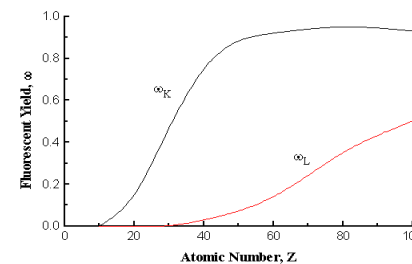


- Internal photoionisation:
- Energy of characteristic X-ray is high enough to eject outer electrons:
  - Reduces XRF intensity
  - The effect is more common in elements of low Z because their atomic electrons are more loosely bound and their characteristic X-rays more readily absorbed.

$$|E_{ae}| = (E_1 - E_2) - E_3$$

19

## Auger Effect: impact on X-Ray yield



The fluorescence yield ( $\omega$ ) = the ratio of X-ray photons emitted from a given shell to the number of vacancies created in that shell.

- The yield of X-ray photons is reduced by the Auger effect.
- Since production of Auger electrons is the only other competing reaction the ratio of Auger electrons to vacancies must be  $1-\omega$ .

20

### 3<sup>rd</sup> year spectroscopy: 2nd Topic

- XRF Instrumentation:

- Sources.
- Detectors
- Energy Dispersive (ED-XRF)
- Wavelength Dispersive (WD-XRF)

- Be able to show an understanding modes of operation of the instruments and components.

21

### X-Ray sources

- X-Ray tubes:

- Hi spec/power, usually bulky & water cooled.
- Lightweight low power for EDXRF

- Radio-nuclides emitting X-rays or low energy  $\gamma$  rays:

- transitions in the nucleus  $\Rightarrow$  gamma rays:
- electron capture  $\Rightarrow$  emission of X-rays
- **Electron capture decay:**  $^{55}\text{Fe}$  (26 p+ & 29 n) captures an (K) orbital electron, resulting in  $^{55}\text{Mn}$  (25 p+ & 30 n) and a K-shell vacancy  $\Rightarrow$  emission of Mn K-L<sub>3,2</sub> or Mn K-M<sub>3,2</sub> X-ray.

- Used for: portable ED-XRF systems that can be operated in the field (*otherwise too much power needed*).

22

### Detectors: three types

- Gas filled detectors:

- Proportional counters, good for low e x-rays.

- Scintillation Counters:

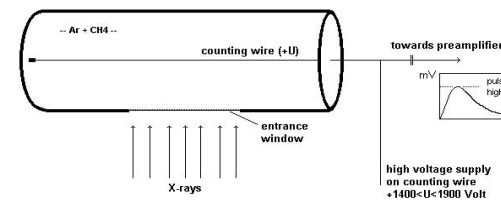
- Better for higher energy x-rays

- Semiconductor detectors:

- Becoming the detector of choice for portable/small systems.

23

### Detectors: gas proportional counter (GPC)



Cylindrical metallic tube in the middle of which a thin wire (counting wire) is mounted.

Tube is filled with a suitable gas (e.g. Ar + 10% CH<sub>4</sub>).

A positive high voltage (+U) is applied to the wire. The tube has a lateral aperture or window that is sealed with a material permeable to X-ray quanta

- An X-ray photon penetrates the window into the counter's gas chamber where it is absorbed by ionizing the gas atoms and molecules.
- Resulting +ve ions move to the cathode (the metallic tube), the free electrons to the anode (the wire).
- The number of electron-ion pairs created is *proportional* to the *energy* of the X-ray photon. To produce an electron-ion pair, approx. 0.03 keV are necessary:
  - radiation of the element boron (0.185 keV) produces approx. 6 pairs
  - and the K $\alpha$  (molybdenum) (17.5 keV) produces approx. 583 pairs.

24

## Detectors: GPC

- Due to the cylinder-geometry arrangement, the primary electrons created in this way "see" an **increasing** electrical field on route to the wire.
- The high voltage in the counting tube is now set so high that the electrons can obtain enough energy from the electrical field in the vicinity of the wire to ionize additional gas particles. An individual electron can thus create up to 10,000 secondary electron-ion pairs.
- The secondary ions moving towards the cathode produce a measurable signal. Without this process of **gas amplification**, signals from boron, for example, with 6 or molybdenum with 583 pairs of charges would not be able to be measured, as they would not be sufficiently discernible from the electronic "noise."
- Gas amplification is adjustable via high voltage in the counting tube and is set higher for measuring boron than for measuring molybdenum. The subsequent pulse electronics supply pulses of voltage whose height depends, among other factors, on the energy of the X-ray quanta.

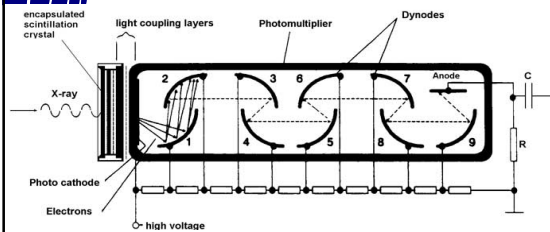
25

## GPC detectors: 2 types

- **Flow counter (FC)**: This is connected to a continuous supply of counting gas (Ar + 10% CH<sub>4</sub>) and has the advantage of being able to be fitted with a very thin window (< 0.6 μm). The FC is therefore also suitable for measuring the very light elements and is very stable.
- The sealed **proportional counter (PC)** has a closed volume and requires a thick window normally made of beryllium:
  - The absorption in this "thick" beryllium window prevents the measurement of the very light elements (Be to Na).

26

## Detectors: Scintillation Counter (SC)



Scintillation crystal: sodium iodide crystal in which thallium atoms are homogeneously distributed "NaI(Tl)." The density of the crystal is sufficiently high to absorb all the XRF high-energy quanta.

- Energy of the X-ray photon is transferred step by step to the crystal atoms that then radiate light and cumulatively produce a flash of light
- The amount of light in this scintillation flash is proportional to the energy that the X-ray photon has passed to the crystal.
- Resulting light strikes a photocathode, easily ejecting electrons. These electrons are accelerated in a photomultiplier and, within an arrangement of dynodes, produce secondary electrons giving a measurable signal.
- Height of the voltage pulse produced is proportional to the energy of the detected X-ray photons.

27

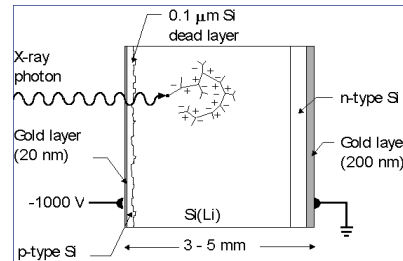
## Detectors: Semiconductor based

- Usually based on a p-i-n-type diode. The diode can only pass an electric current in one direction (rectification mechanism).
- When a voltage is applied against the current (reverse bias) and light is allowed to enter, electrons are excited into a conductive band and only the current for the excited electrons will travel.
- X-ray detection is performed by measuring, one by one, each current pulse that corresponds to an incident X-ray photon.
- **The instantaneous current value of a single pulse is proportional to the incident X-ray energy:**
  - X-ray energy can be found by measuring the pulse height of the current pulse.
- 2 general types:
- Si-Li drift and PIN diode

28

## Detectors: semiconductor, Si-Li drift.

- **Lithium-Drifted Si(Li) Detectors**
- A lithium-drifted Si(Li) detector is manufactured from high-purity p-type silica with lithium, an n-type dopant, is diffused into the material. The lithium atoms compensate for the extrinsic charge-carriers in the p-type silicon and provide a wide "intrinsic" region of high resistance.
- Si(Li) detectors are operated at 77 K with a liquid N<sub>2</sub> cryostat to prevent further diffusion and to reduce the level of random noise due to the thermal motion of charge carriers.
- One electron-hole ~ 3.85 eV

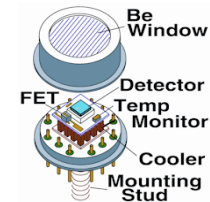


Area: 30-100 mm<sup>2</sup> / Thickness 3-5 mm  
Resolution ~150 eV @ Mn K $\alpha$



29

## Detectors: semiconductor, Si-PIN diodes



Area 5 - 10 mm<sup>2</sup>,  
Thickness ~0.5 mm  
Resolution: ~149 eV @ Fe K $\alpha$ .

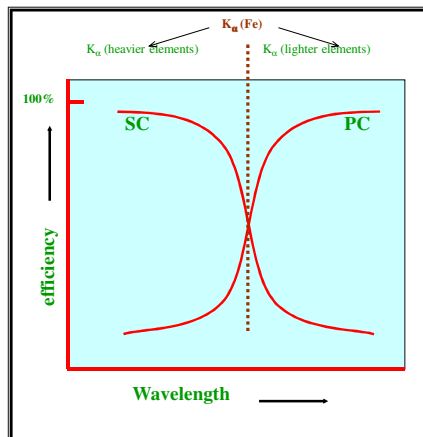


- Very common in ED-XRF
- No liquid N<sub>2</sub> needed / thermoelectric cooling.
- Solid state electronics so compact design.
- Good for detecting X-Rays below 25 keV.

<http://www.amptek.com/x123.html>

30

## Scintillation versus Proportional



- PC detectors better for longer wavelength (lower E) X-ray detection e.g. lighter elements.
  - For the GPC the shorter wavelength X-rays pass thru without being absorbed.
- SC detectors better for shorter wavelength (higher E) X-ray detection e.g. heavier elements.

## Detectors: signal processing

- Detectors produce output pulses:
  - Usually a voltage, height  $\propto$  signal.
- Have to be amplified, counted, analysed.
- Multichannel analyzers:
  - Number of pulses = number of x-rays
  - Pulse height = energy of the x-ray

32

## Signal Analysis: multichannel analyser

- The pulse goes to the data acquisition system which is usually an electronic device called MCA (Multi-Channel Analyzer) where it is processed.
  - An MCA is akin to a computer memory where each memory address is here called a "channel". Each channel is in fact a counter of the numbers of impulse of a specific height (& thus energy) submitted to the MCA unit.
  - Lots of different types, PCI boards & USB units.

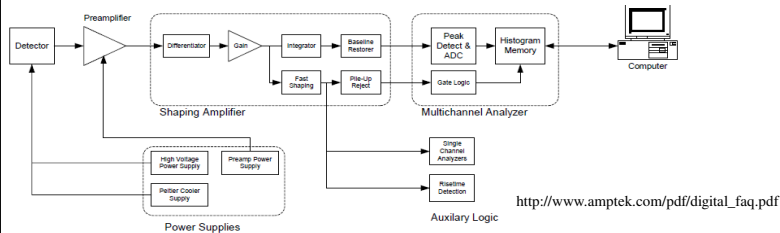


Figure 1. Block diagram of a traditional analog spectroscopy system. In addition to the detector and preamplifier, it includes a shaping amplifier, an MCA, power supplies, and auxiliary logic function. These are generally separate modules.

33

## XRF Spectrometers

- Wavelength Dispersive WD-XRF:
  - Energy of XRF output is measured by physical separation of the emission wavelengths.
- Energy Dispersive ED-XRF:
  - Energy of XRF output is electronically measured by the detector.
  - Many different types
    - Secondary reflection
    - Total Reflection XRF (TXRF).
    - Radio-isotope ex..
    - Mars Rover.
- Two main types:
  - Single channel (sequential)
  - Multi-Channel (simultaneous)

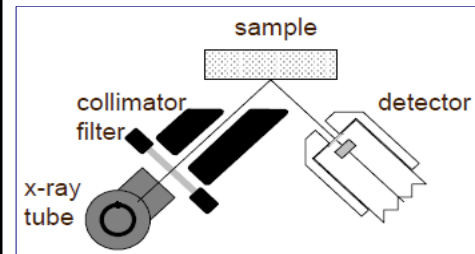
34

## Energy-Dispersive spectrometers

- The core of an ED-spectrometer is a semi-conductor crystal (Si, HPGe) a high voltage is applied over the crystal (bias  $-5/600$  V) and the crystal is cooled (e.g. using LN2 or Peltier):
  - When x-rays enter the crystal electron-hole pairs are formed the number is proportional to the energy of the x-ray because of the bias the electrons are swept out of the crystal.
  - For each photon an electric pulse is produced with an amplitude proportional to the energy
  - Measuring the pulse amplitude and counting no. of pulses produces the ED-spectrum

35

## Energy Dispersive (ED) spectrometer I

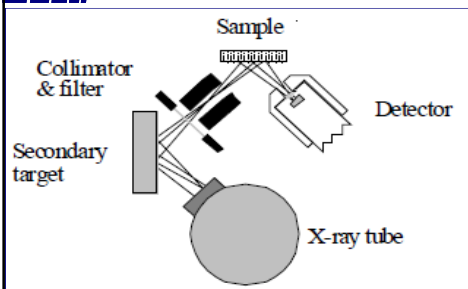


- Direct excitation:
  - Mechanically very simple.
  - Can be very compact.

- Basic Design:
  - X-Ray tube, Collimator, Sample holder
  - Detector, MCA, Computer & Software.
- Uses PC detectors (Si-Li, Si-PIN) to separate the X-ray photons according to their energy.
- Measures all elements within its range at the same time.

36

## ED-XRF: Secondary target excitation

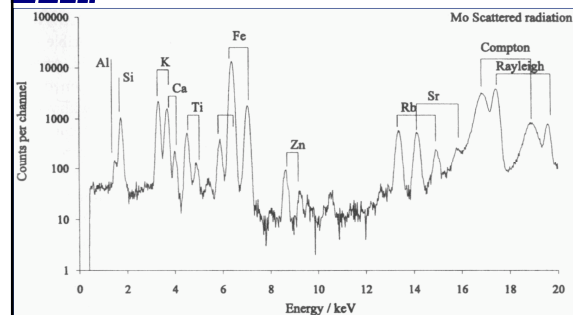


- Cleaner X-ray source for excitation of sample.
- Continuum largely removed.
- Lower spectral background, better detection limits.

- Uses different metal targets:
  - Wider range of discrete excitation wavelengths (*quasi-monochromatic*).
  - Optimal excitation for specific elements.

37

## ED-XRF: Secondary target excitation



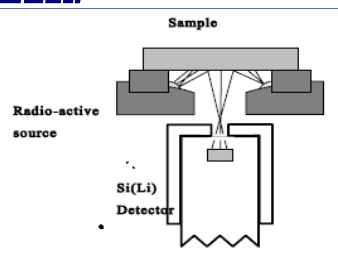
- Mo Secondary target:
  - $K_{\alpha}/K_{\beta}$  EX
  - 16-20 keV peaks due to scattering.

- Spectrum of geological standard (JG1): *Geological Survey of Japan*
  - 3000 sec. exposure

p. 687, Analytical Chemistry: A modern Approach.....

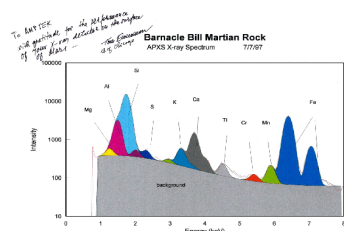
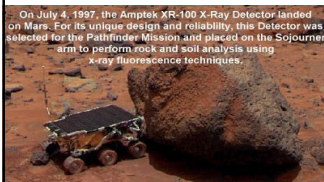
38

## ED-XRF: Radio-isotope excitation



- For handheld systems
- Used on Mars Pathfinder:
- Very compact
- Don't need much energy

- Alpha Particle X-Ray Spectrometer (APXS): <http://www.amptek.com/press.html#pathfinder>

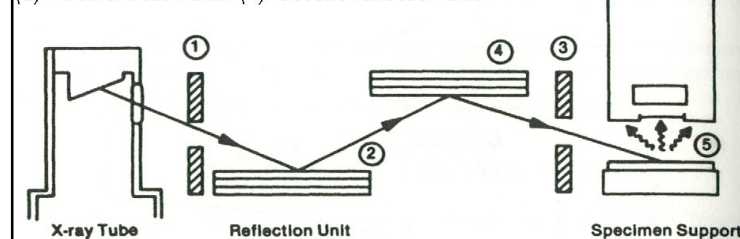


39

## ED-XRF: Total Reflection XRF

(1 & 3): Apertures / (5): sample.

(2): First reflection unit / (4): Second reflection unit.



Low Glancing angle, means less scattering & more absorption.

- Detector very close (~5 mm) to sample.
- Used for thin film analysis, <mg amounts of sample.

40

## TR-XRF

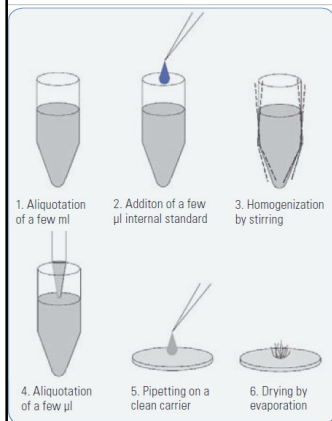


Figure 4: Sample preparation steps for the TXRF analysis of liquids

[http://www.bruker-axs.de/uploads/tx\\_linkselectorforpdfpool/LR\\_XRF\\_426\\_S2\\_PICOFOX\\_TXRF\\_Principles\\_low\\_res.pdf](http://www.bruker-axs.de/uploads/tx_linkselectorforpdfpool/LR_XRF_426_S2_PICOFOX_TXRF_Principles_low_res.pdf)

### Advantages:

- Glancing the primary x-ray beam from a pure optical surface totally eliminates background due to the primary beam.
- Extremely low detection limits are achievable.
- Sample may be a drop of water evaporated onto the quartz surface.
- Lab Report XRF 426



41

## Typical ED-XRF: NBL system



- ~50K€ COST
- Benchtop design
- Autosampler & spinning.
- Low power x-ray tubes.
- two detectors:
  - Semiconductor based.



Bruker, S1 handheld:  
Ag Target, 40 kV:  
- *In-situ* Scrap metal analysis

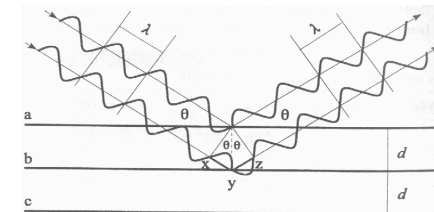
42

## Advantages of ED-XRF

- Simple instrumentation: no moving parts.
- Relatively low cost instrumentation.
- Can be made portable & handheld.
- A range of alternative excitation sources can be used in place of high-power x-ray tubes with their large, heavy, expensive and power-consuming supplies:
  - low power x-ray tubes, secondary monochromatic radiators, radioisotopes and ion beams.
- Simultaneous accumulation of the entire X-ray spectrum
- Fast qualitative analysis (30 s, or so).

43

## Wavelength Dispersive



- Based on Bragg diffraction:  $2d \sin \theta = n \lambda$  ( $n=1,2,\dots$ ):
- the x-rays reflected from the second plane (b) travel a distance  $xyz = 2d \sin \theta$  further.
- Get constructive interference when diff. = integer no. of wavelengths (destructive otherwise).

44

### WD-XRF schematic

- Secondary X-ray photons from the sample strike the crystal.....
- Angle  $\theta$  varied by physical rotation.
- Use Flow proportional or scintillation counters to detect x-rays
- Plot intensity versus  $2\theta$ .
- Crystal chamber usually under vacuum.

[http://users.skynet.be/xray\\_corner/xtb/chap011.html](http://users.skynet.be/xray_corner/xtb/chap011.html)

### WD-XRF: Crystal Selection

Crystal and plane	$2d$ (nm)	wave-length range (Å)	Typical element range
LiF (200)	0.402	3.88 - 0.52	K - Cd (K-lines)
Lithium fluoride			Sn - U (L-lines)
PET (002)	0.874	8.44 - 1.14	Al - Cl
Pentaerythritol			

- Use different crystals for different wavelength ranges: *Crystallographic plane separation, d.*
- For XRF spectrometer use  $d$  (inter-planar spacing) is constant and  $\lambda$  (wavelength) is the variable.

### WD-XRF spectrum

WD spectrum of a geological material between 0.69 and 0.98 Å

- High resolution, very little peak overlap.
  - 100-1000 ppm.
- Sequential (i.e. scanning) measurement ....so it is a slow measurement.

p. 683, Kellner.

### EDXRF vs WDXRF

- Higher energy (spectral) Resolution:
  - WDXRF: 5 eV to 20 eV.
    - Depending on set up
  - EDXRF; 150 eV to 300 eV or more:
    - Depends on detector used.
- High resolution WDXRF good for reducing spectral overlaps & allows for more accurate analysis of complex samples.
- In addition, with high resolution backgrounds are reduced, providing improved detection limits and sensitivity.
- But: the extra optical components in WDXRF (e.g. diffracting crystal & collimators) greatly reduces efficiency:
  - Compensate by using high powered X-Ray sources, but this increases cost & complexity, which can have a significant impact on ease of use / cost of ownership.

## Energy vs. Wavelength Dispersion

- Energy Dispersion:
  - all energies measured simultaneously
  - Fast
  - Higher sensitivity
  - Low resolution
  - Less expensive
  - Portable instruments with low intensity sources
- Wavelength Dispersion:
  - Scan emission wavelength with a crystal
  - Slow
  - High resolution
  - More expensive
  - Physically larger

49

## Sample Handling: instrumentation

- Sample spinner:
  - Used to smooth out the influence of sample orientation: generates reproducible observed intensities for samples & standards.
- Multi-sample holder:
  - To enable large sample numbers, most systems have carousels for .....
- Bespoke: systems can be adapted for a wide variety of in-situ analyses: e.g. mars rover



50

## XRF: Sampling

- XRF Sampling Spectroscopy:
  - Quantitative method
  - Solids
  - Liquids.
  - Calibration standards
- Key Principle:
  - Calibration & test samples should have the same physical properties..

51

## Quantitative method

- XRF widely used for quantitative analysis of elements in mixtures. Procedure a bit like *UV-VIS/Beer-Lambert*:
  - Design experiment (what to quantify & in what form).
  - Generate a calibration sample set.
  - Collect XRF data from the calibration samples.
  - Build a linear calibration model:
    - peak intensity versus concentration – select a specific XRF line.
  - Collect XRF spectra from unknown (test) materials.
  - Use calibration model to predict concentration.
- Calibration & test samples should be identical in physical form & have similar chemical compositions.

52

## Solids Preparation: metals

- **Usually prepared as solid disks:**
  - Conventional machining: cutting, milling and polishing. Grinding used for hard alloys and brittle materials (ceramics).
  - **Polishing** require needed to produce scratch-free surface necessary for most analyses, and a mirror-like surface if light element analysis required.
  - Mechanical polishing may be undesirable for soft, malleable, multiphase alloys because of smearing of the softer components. The intensities of the elements in softer phases increase while those of the harder phases decrease.
  - Polishing may be a source of contamination since common abrasives (SiC & Al<sub>2</sub>O<sub>3</sub>), contain elements that are often determined in commercial assays. Sample surface cleaning may be necessary to remove contamination as well as grease and handling residue.

53

## Solids Preparation: powders I

- For powders macroscale heterogeneity & particle size effects can be important.
  - Variations in density etc.
- Thus it is usual to grind powders/solids to get a uniform distribution.
  - Use a ball mill, mortar & pestle
  - Although inhomogeneity and particle size can often be minimized by grinding and pelletizing at high pressure, often the effects cannot be completely removed because the harder compounds present in a particular matrix are not broken down. These effects produce systematic errors in the analysis of specific type of material, such as siliceous compounds in slags, sinters and certain minerals.

54

## Solids Preparation: powders

- **Pressed Pellets: *quickest and simplest method***
  - press the powders directly into pellets of *equal density*, with or without the use of a binder.
  - In general, provided that the powder particles are less than about 50 μm in diameter, the sample will pelletize at 10 to 30 t.
  - Where the self-binding properties of the powder are poor, use higher pressure or use a binder (e.g. was, ethyl cellulose, boric acid).
  - The binder must be:
    - » free from significant contaminant elements, must have low absorption, be stable under vacuum and irradiation conditions, and it must not introduce significant interelement interferences.



55

## Pressed pellets: equipment

- Need a Hydraulic press & Die set:
  - 30-40 Ton Press.
  - 25 to 35 mm dies (large samples):  
Need to produce good quality pressed powder samples.
- Analytical data for longer wavelengths will sometimes be improved if a finely ground powder is compacted at higher pressures (say up to 30 t).
  - A 40-ton press should be therefore considered if light element analysis is required in pressed powder samples.
- Powders can be pressed into aluminum cups or steel rings.
- Alternatively boric acid backing can be used, or free pressing if a binder is used.



<http://www.youtube.com/watch?v=KHqrKIDsEXQ>

56

## Solids: Fused Beads

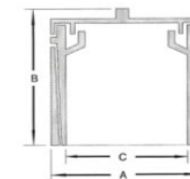
- The dissolution or decomposition of a portion of the sample by a flux (e.g. borates, like sodium tetraborate, lithium tetraborate and lithium metaborate) and fusion into a homogeneous glass eliminates particle size and mineralogical effects entirely.
- Heat sample-flux mixture at 800 to 1200 °C so that the flux melts & sample dissolves. Composition and cooling conditions must be such that a one-phase glass is produced.
  - Use platinum alloy or graphite crucibles.
- Additional advantages:
  - Possibility of high or low specimen dilution to decrease matrix effects
  - Possibility of adding compounds such as heavy absorbers or internal standards to decrease or compensate for matrix effects
  - Possibility of preparing standards of desired composition

<http://www.youtube.com/watch?v=GXqnhfn18GU>

57

## Liquids:

- Use a sample cup with a thin Mylar film window base.



- The Mylar (Polyethylene terephthalate (PET).) film is stretched over the base of the sample cup and held in place by an outside sleeve.
  - Mylar is ~2.5 to 6 µm thick
  - Reasonably chemically resistant.
  - Low levels of other elements.

**Typical application:**  
Sulphur in petroleum:  
*1 to 100 ppm range*

<http://www.xrf-supplies.com/>

58

## Calibration Standards 1

- As a result of absorption and enhancement effects, standards, in general, must mimic the matrix of the material being analysed as closely as possible:
  - all background elements present in the material being analysed must be included in the standards and,
  - as far as possible, with matching concentrations.
  - have the same physical size/properties.
- In many cases standards can be bought in.

59

## Calibration samples: solutions

- In the case of solutions, the components of the solution being analysed must appear in the standard solutions (as is the case for solids) but,
- unlike the situation with solids, there is no problem in achieving homogeneity.
- However, may also need to use specialist sample holders & take precautions to avoid evaporation.

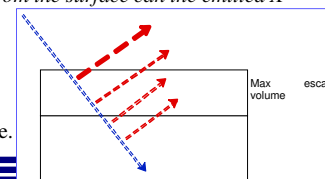
## Matrix effects

- XRF Sampling Spectroscopy:
  - Penetration Depths
  - Absorption: *the Mass Attenuation Coefficient*
  - Secondary emission / enhancement
- Understand and be able to explain Raman spectroscopy and the selection rules. Describe the instrumentation and the pros/cons of the method.
  - Sec. 19.12 & 19.15 Elements of Physical Chemistry, 4<sup>th</sup> ed.
  - Sec. 13.13 & 13.16: Physical Chemistry, 8<sup>th</sup> ed. Atkins.
  - Chapt.4, Fundamentals of molecular spectroscopy, Banwell & McCash.

61

## Penetration Depth

- Penetration depth in a material is dictated by several factors:
  - **X-Ray wavelength:** Long wavelengths are of relatively low energy and are least penetrating (soft x-rays).
  - **Coefficient of absorption,  $\mu$ ,** of the material for the wavelength in question. The value of  $\mu$  is dictated by the chemical composition.
    - › High atomic weight atoms such as barium and lead give rise to large values of  $\mu$  and it is for this reason that they are employed as protective screens against x-rays.
- Have to consider two elements:
  - The excitation X-Ray photons: *how far into the sample can we excite XRF?*
  - The emitted X-Rays of the analytes? *How far from the surface can the emitted X-Rays escape to the detector?*
- Have to design this in to the analytical method:
  - Appropriate calibration standards for the sample.



62

## Absorption I

- Passing through matter weakens the intensity of X-rays:
  - Depends on both the radiation energy and sample chemical composition:
    - › Heavier elements absorb better than light ones: 1 mm of lead absorbs practically all of the higher-energy radiation occurring during XRF, whereas 1 mm of polypropylene is more or less permeable to X-rays.
    - › Low-energy/long wavelength X-ray photons are absorbed more readily than quanta with higher energy:
    - › E.g. the  $K\alpha$  photons emitted by boron, have a very low energy of 0.185 keV (= 67 nm) and are almost completely absorbed by even 6  $\mu\text{m}$  of polypropylene foil.
- This is critical for the analytical application of XRF:  
*one has to consider samples & containers*

63

## Absorption II

- If an X-ray with quanta of energy E and an intensity of  $I_0$  pass through a layer of material, the ray emerging from behind the layer will only be left with the intensity  $I_t < I_0$  as a result of the absorption:
  - The relationship between I and  $I_0$  after the transition through a layer of thickness  $d$  & density  $\rho$  is described by the law of absorption:

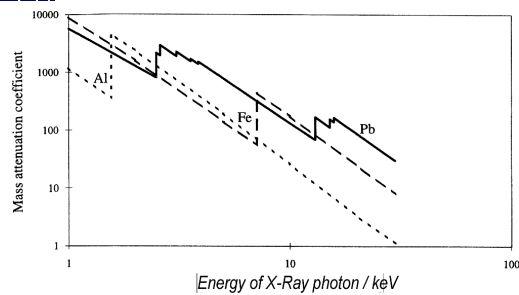
$$I_t = I_0 e^{-\mu\rho d},$$

$\mu$  = mass attenuation co-efficient [units of  $\text{cm}^2\text{g}^{-1}$ ].

- $\mu$  related to energy of incoming x-rays, cross-section for photo-electric absorption, elastic & inelastic scatter, & nature of the atoms in the sample.

64

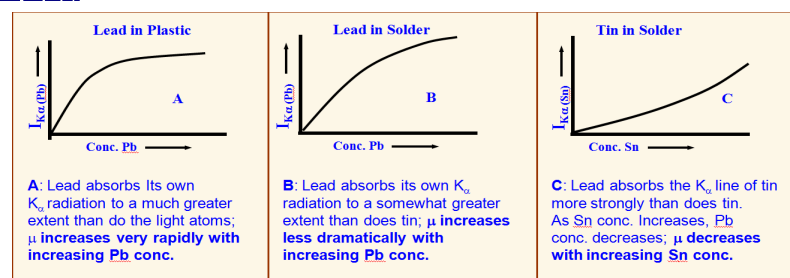
## Mass attenuation co-efficient



- The mass attenuation coefficient,  $\mu$ , has the dimension  $[\text{cm}^2/\text{g}]$  and only depends on the atomic number of the absorber element and the energy/wavelength, of the X-rays.
- Have to be careful about primary & secondary wavelengths.

65

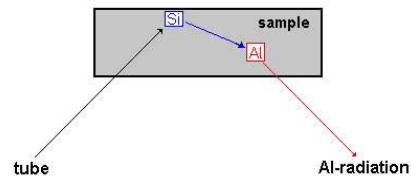
## Absorption effects



- As Pb. conc. in an otherwise light element matrix increases:
  - coefficient of absorption of the matrix increases at a much greater rate as shown in the above;
  - in general, the concentration of a component in a matrix is not linearly related to the value of  $\mu$  for the matrix thus accounting for non-linear calibration plots.

66

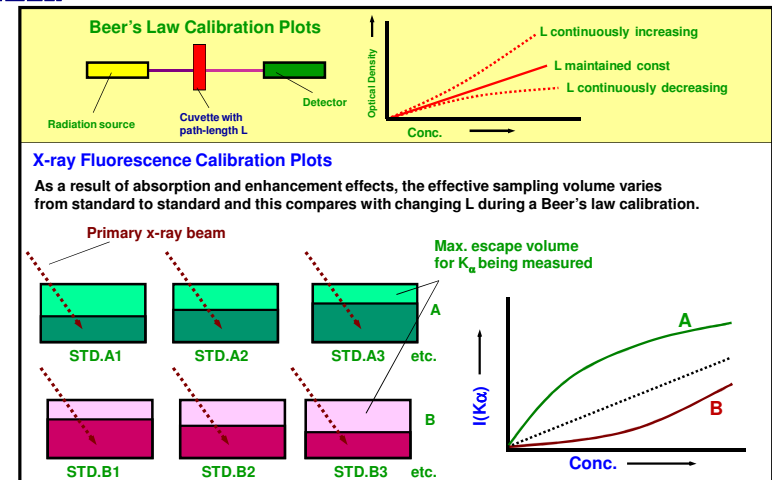
## Intensity Enhancement



- X-rays produced by one component in the sample are energetic enough to cause XRF in another component in the sample.
- **Example:**
  - A Si  $K\alpha_1$  photon is produced in a sample by the primary excitation source.
  - Inside the sample, it can be absorbed again by transferring its energy to an Al K electron.
  - This can then emit an X-ray quantum itself.
  - The Si radiation thus contributes to the X-ray emission of the aluminium.

67

## Beer-Lambert vs. XRF calibration plots

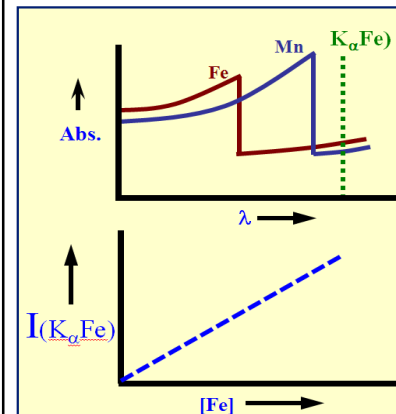


## Absorption effects: edge diagrams

- If we consider three different types of steel:
  - Manganese steel (Fe-Mn)
  - Fe-Cr alloy
  - Nickel Steel (Fe-Ni)
- What effect does the presence of the other element have on the XRF calibration plots?
- As the x-ray wavelength increases, each element will absorb the radiation more effectively.
- Furthermore, each element has an absorption edge and the edge occurs at a different wavelength for each element.
- The positions of absorption edges profoundly effect the form of calibration plots.

69

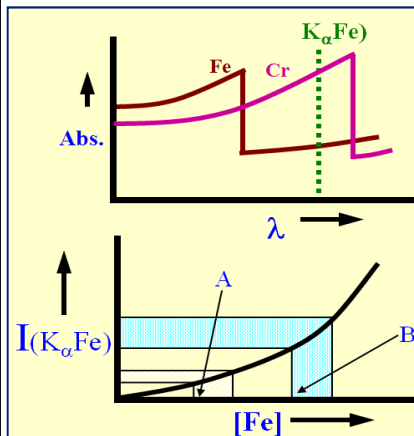
## Fe-Mn: minimum impact



- At the wavelength of the  $K_{\alpha}$  line of iron, manganese and iron absorb almost equally.
- Therefore, the value of  $\mu$  (at this wavelength) for the alloy is almost independent of iron/manganese composition
- Hence a linear calibration plot.

70

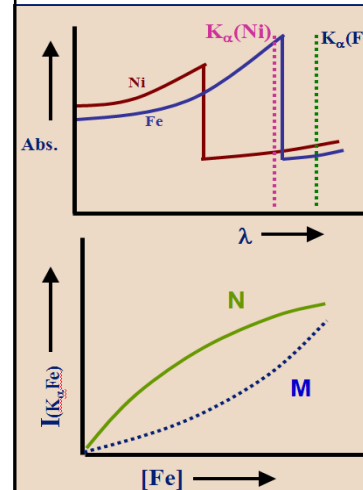
## Absorption effect: Fe-Cr alloy



- Cr absorbs the  $K_{\alpha}$  line of iron much more strongly than does Fe.
- At the point A the steel is richer in Cr than at point B.
- Thus, an incremental increase in iron conc. at point A results in a smaller increase in intensity of  $K_{\alpha}$  than at point B.
- The coefficient of absorption is greater for iron  $K_{\alpha}$  radiation at A than at B.

71

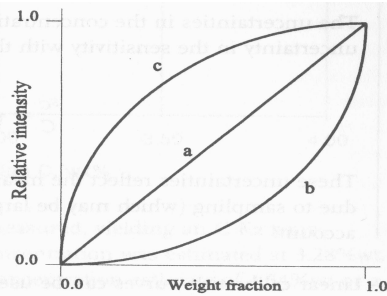
## Intensity Enhancement (Fe-Ni case)



- If an element A of a matrix has its  $K_{\alpha}$  line directly behind the absorption edge of an element B (i.e. to the high energy side of the absorption edge), the intensity of the  $K_{\alpha}$  line of B will be enhanced by A.
- For nickel steel: M would be the predicted calibration plot if only absorption effects alone were occurring.
  - But, Ni  $K_{\alpha}$  line is directly to the high energy side of the absorption edge of iron,
  - The iron  $K_{\alpha}$  signal intensity is enhanced by nickel.
  - Enhancement effect is greatest when Fe conc. is low and Ni conc. is high
  - So we get the calibration curve N.

72

### Effect on calibration plots



- Possible relationships between peak intensity (for a specific x-ray) and sample concentration:

- (a): No absorption & no enhancement effects.
- (b): Absorption effects only.
- (c): Enhancement effects only.

73

### Advantages of XRF (1)

- It is a non-destructive technique.
- All elements from Be to U can be determined and interference generally is not a problem.
- Analysis can be in the ppm range but can equally be in the high concentration range (e.g. greater than 90%) without the need for dilution.
- 1 % relative error routinely, 0.1 % with care and corrections
- Samples for analysis can be in the liquid or solid state and often can be analysed as received:
  - Analysis can be carried directly on creams, greases, finely dispersed powders, metals, glasses, ceramics or plastics.
  - Analysis can be carried out on irregular shaped objects.

74

### Advantages of XRF (2)

- It is an environmentally friendly technique (very little solvent use etc.).
- Modern instruments are relatively cheap & compact (portable instruments are available).
- High throughput of samples is possible with automation.
- Multi-element analysis can be performed on each sample.
- It is a fast technique:
  - There are few analytical techniques that can match XRF for speed because a very large number of samples can be preloaded and multi-element analysis carried out on each. Furthermore, analysis time for each sample is reasonably fast (seconds to minutes).
- Qualitative analysis (comparing spectra) is exceptionally fast.

75

### Disadvantages of XRF

- Uses X-Rays/Radioactive sources:
  - so have to use special operations/ H&S requirements.
- Not great for light elements.
- Not so good for trace analysis:
  - AA/ICP-MS better for ppb etc..
- Needs a lot of sample preparation sometimes.
- Needs calibration samples.

76