Total reflection of X-rays

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How XRF works

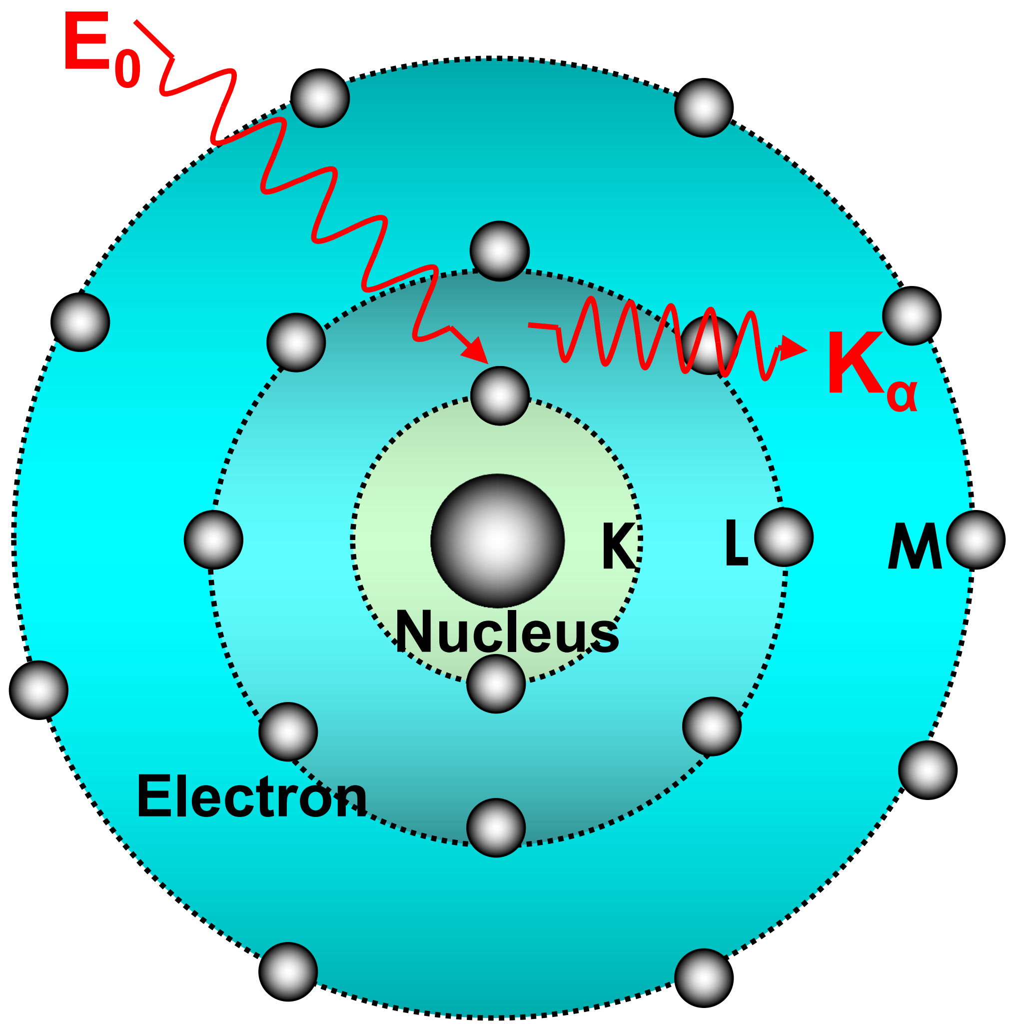
Working principle:

1) Photo-Ionization of **atomic bound** electrons (K, L, M)

2) emission of photo-electron

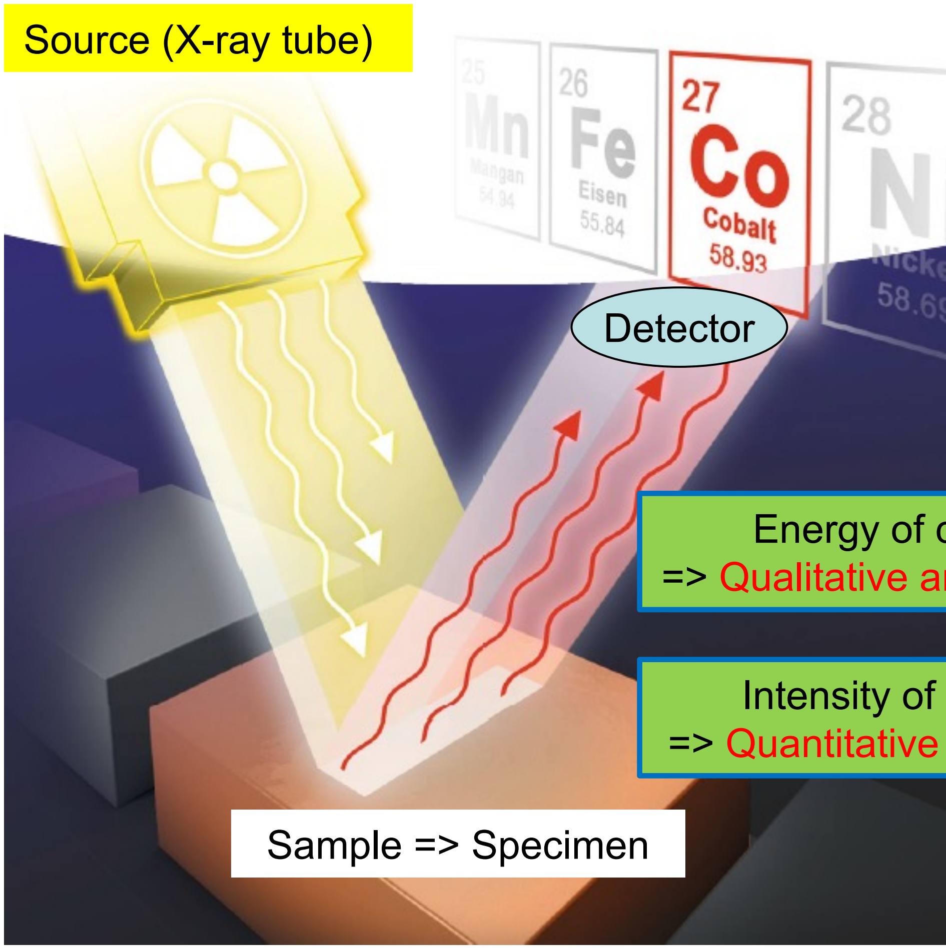
3) => electron from higher shell fills this position

4) Emission of element "**characteristic**" **fluorescence** X-rays



Energy E_0 must be adequate to expel bound electrons:
E_0 > Binding energy of respective shell (K, L, M)

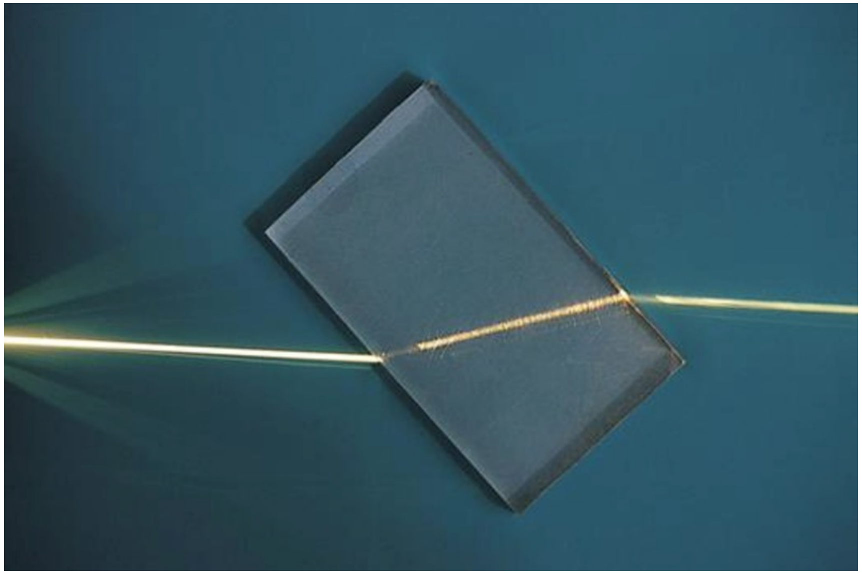
How XRF works



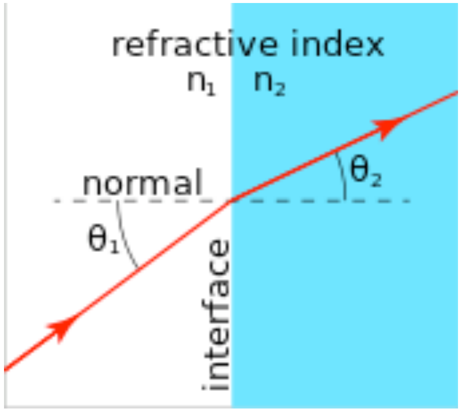
Energy of characteristic X-rays
=> Qualitative analysis (chem. Elements)

Intensity of characteristic X-rays
=> Quantitative analysis (Concentration)

Light in the visible range



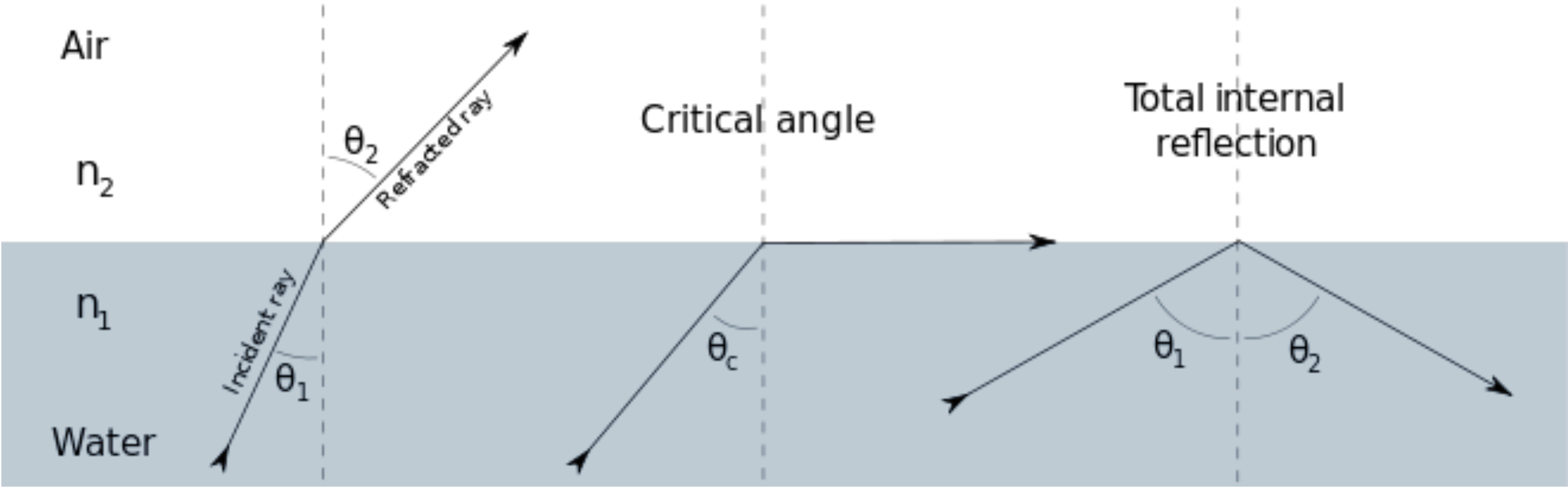
A ray of light being refracted in a plastic block.

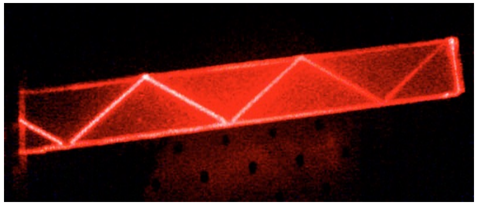


Refraction of a light ray.

$$\frac{\sin\theta_2}{\sin\theta_1} = \frac{v_2}{v_1} = \frac{n_1}{n_2}$$

Refraction – total reflection (visible light)





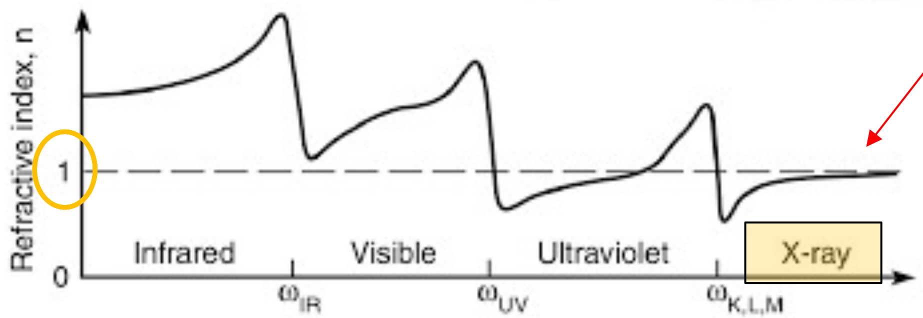
$$\frac{\sin\theta_2}{\sin\theta_1} = \frac{v_2}{v_1} = \frac{n_1}{n_2}$$

$$n_1 > 1$$
$$n_2 = 1$$

Refraction of light at the interface between two media, including total internal reflection.

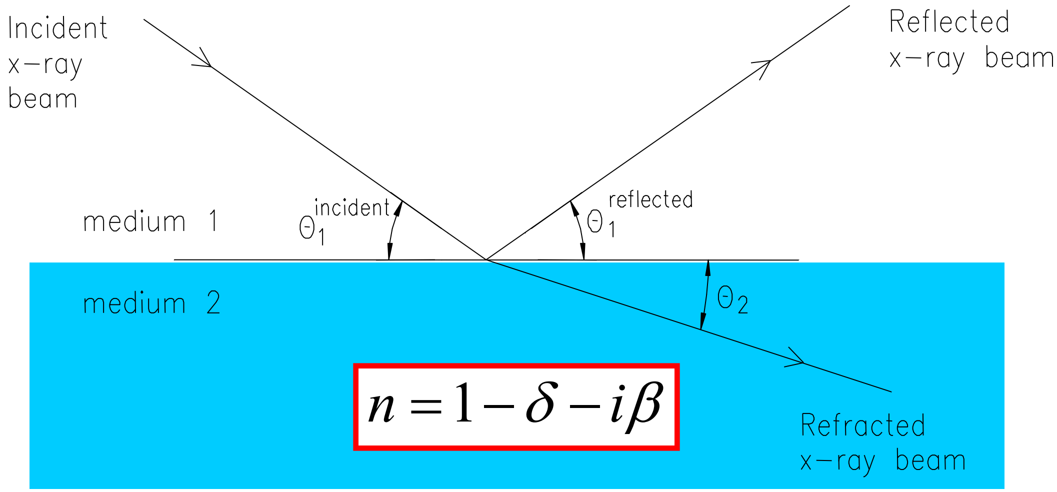
Refractive index for X-rays

$$n = 1 - \delta - i\beta$$



n < 1 for X-rays
e.g.: 0.999995

Total (external) reflection of X-rays



Deviating definition of angles

$$\varphi_{Si}^{crit}(\mathrm{mrad}) \approx \sqrt{2 \cdot \delta} \approx \frac{32.2}{E_0(\mathrm{keV})}$$

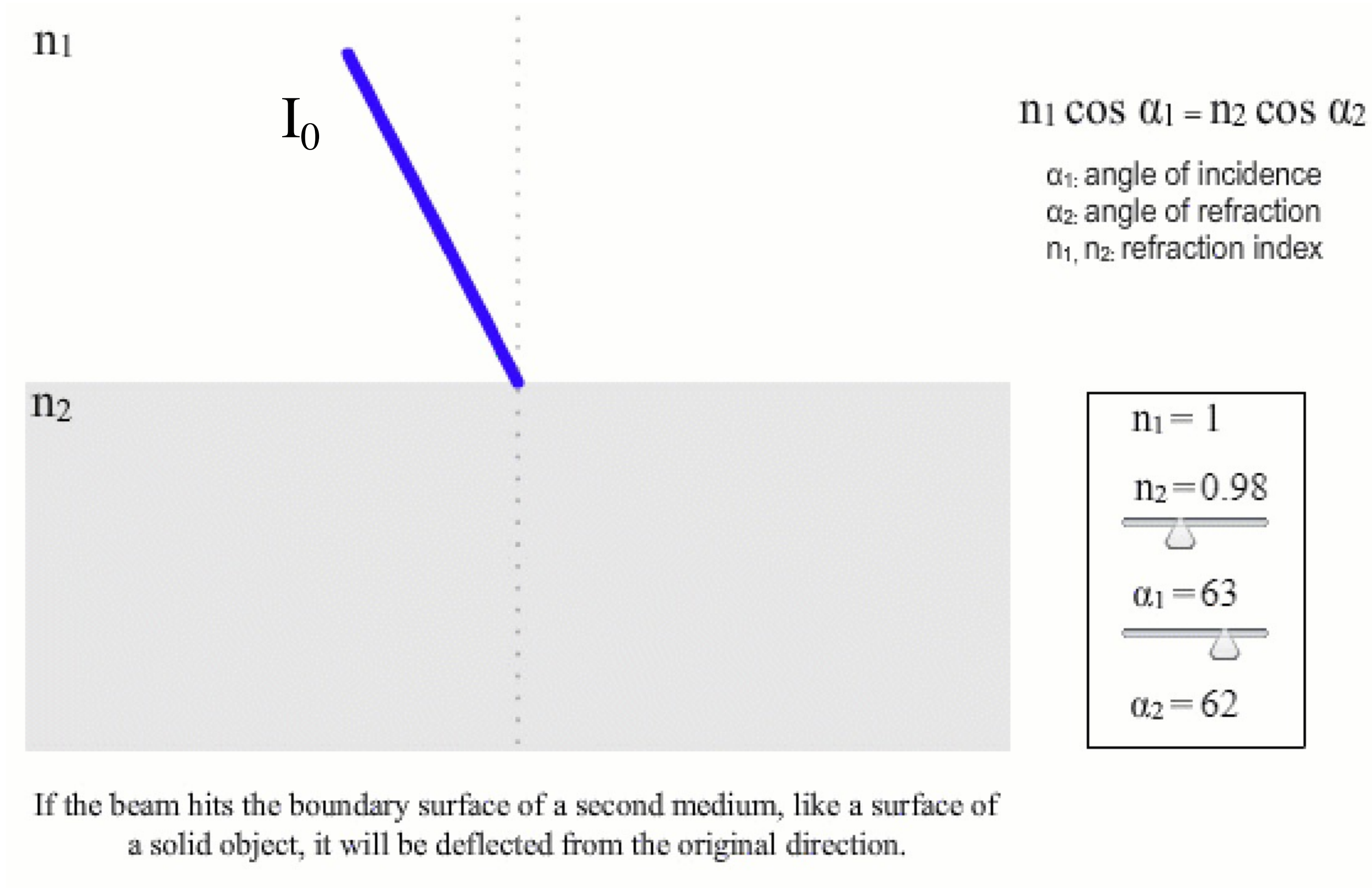
X-ray range:

$\delta \sim 10^{-6}$ … dispersion (coherent scatter)

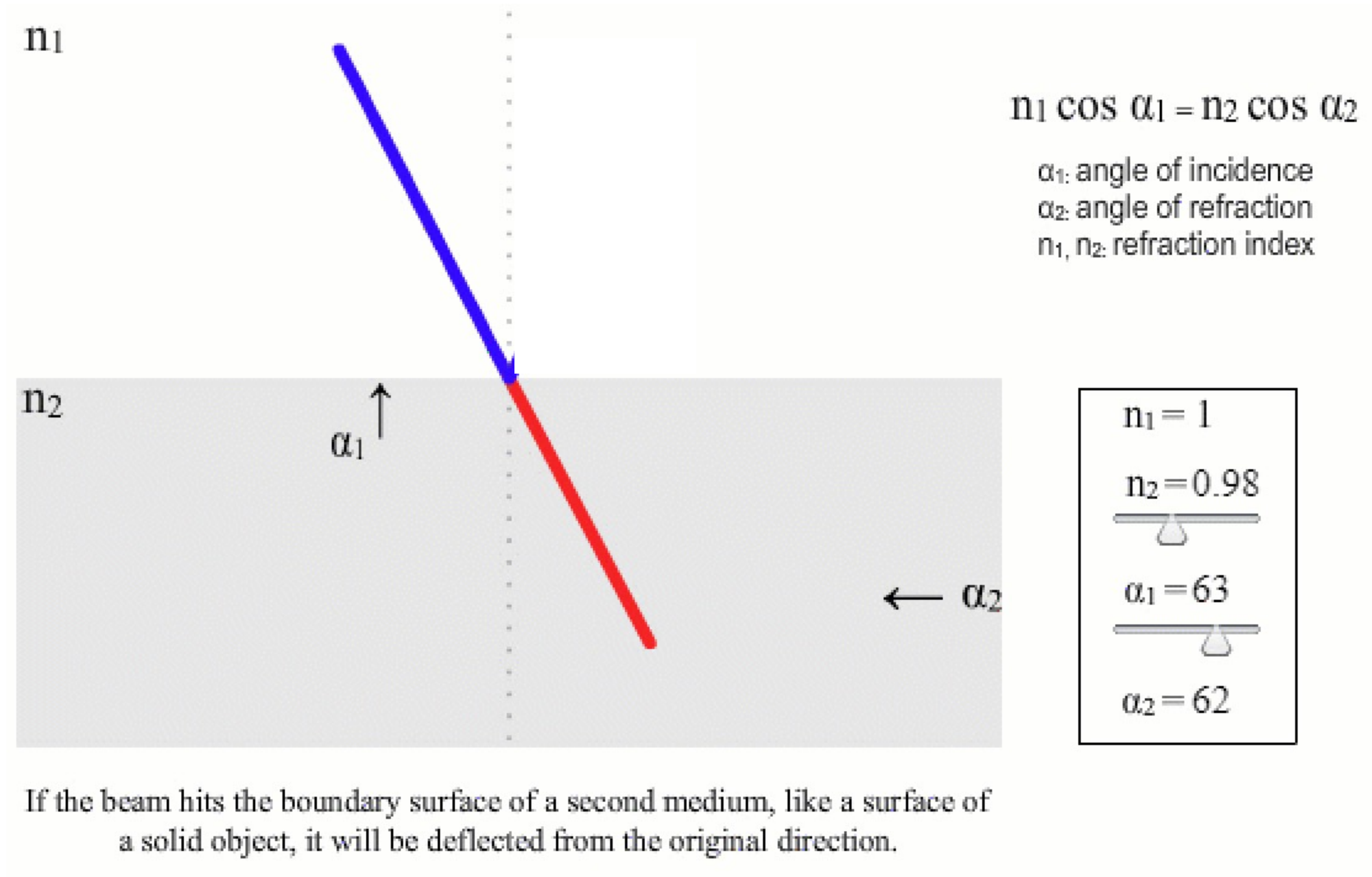
$\beta \sim 10^{-8}$ … absorption

Quartz reflector, E_0 = 17.5 keV: ≈ 0.1° ≈ 1.75 mrad

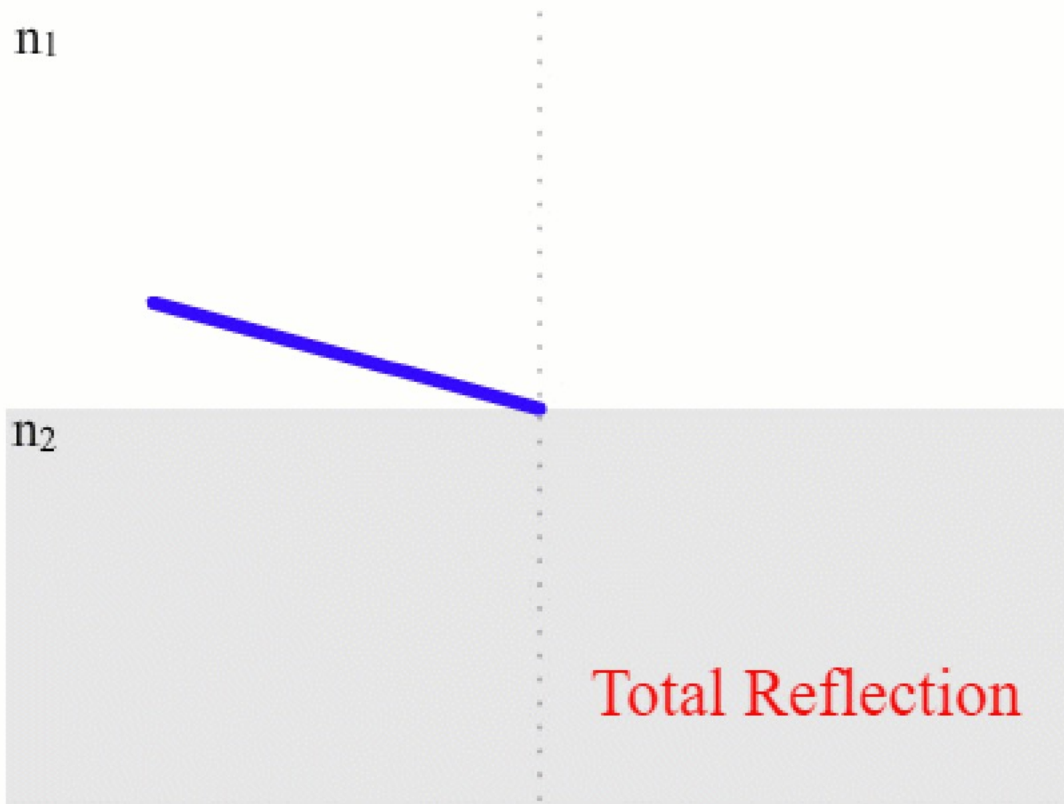
total reflection condition not fulfilled



Interaction with medium



TXRF condition fulfilled



$$n_1 \cos \alpha_1 = n_2 \cos \alpha_2$$

α_1: angle of incidence
α_2: angle of refraction
n_1, n_2: refraction index

$n_1 = 1$

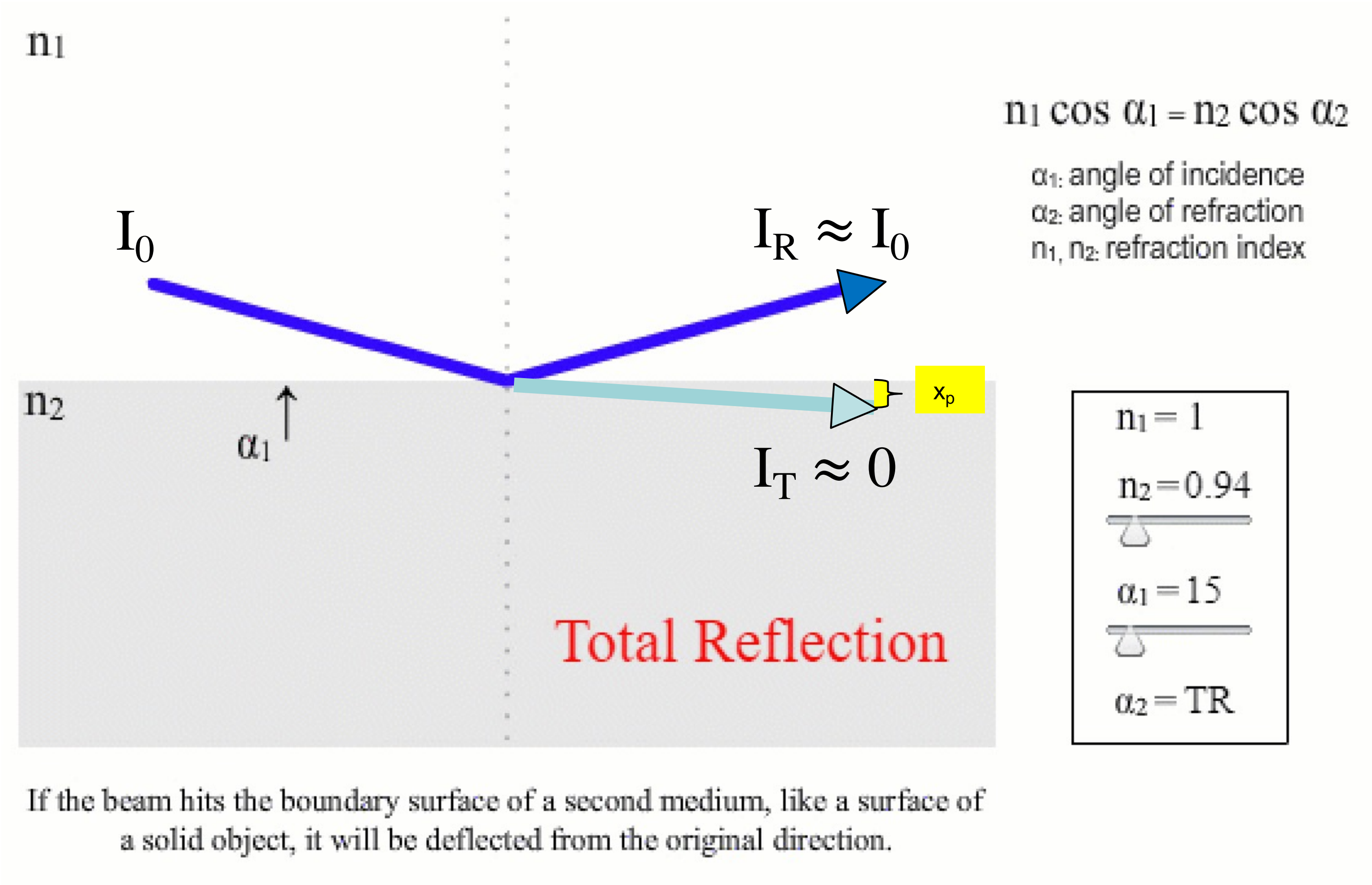
$n_2 = 0.94$

$\alpha_1 = 15$

$\alpha_2 = TR$

If the beam hits the boundary surface of a second medium, like a surface of a solid object, it will be deflected from the original direction.

Animation



x_p … penetration depth

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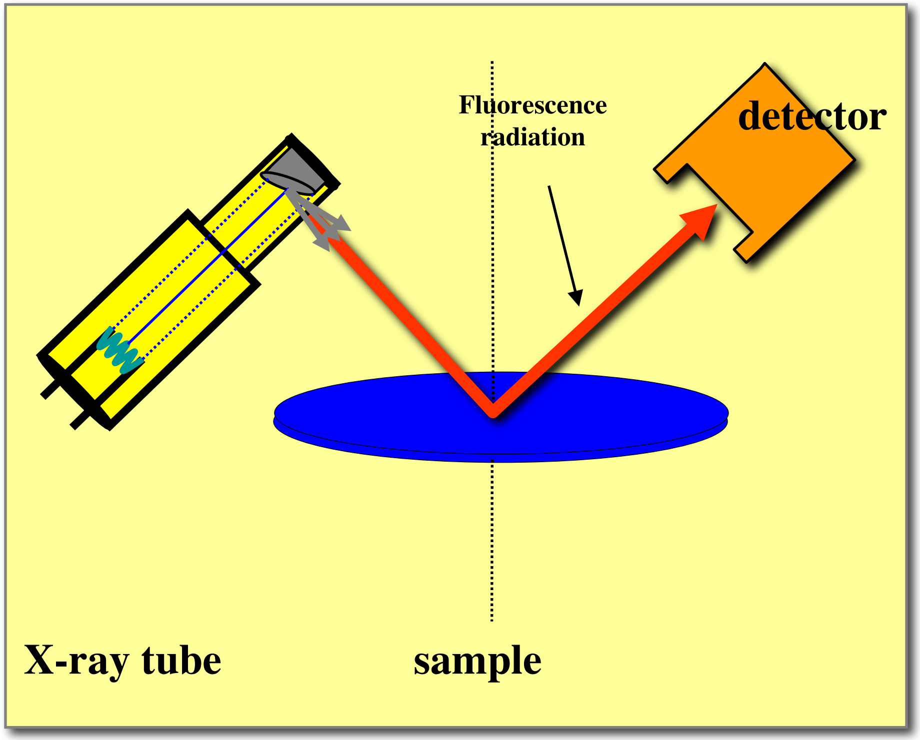
Total reflection X-ray Fluorescence Analysis

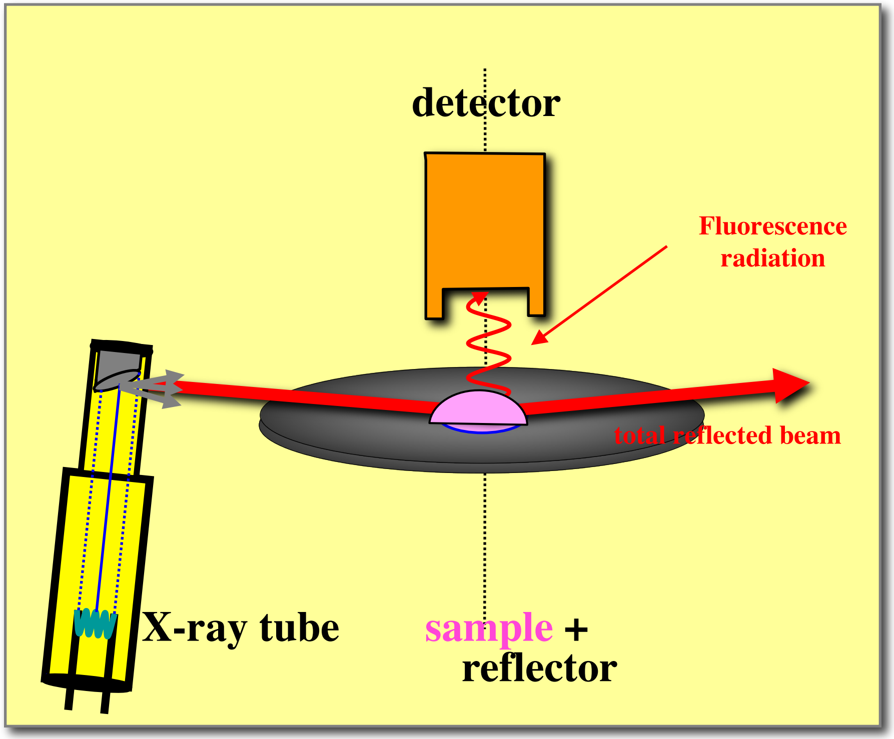
TXRF

Principle of XRF and TXRF

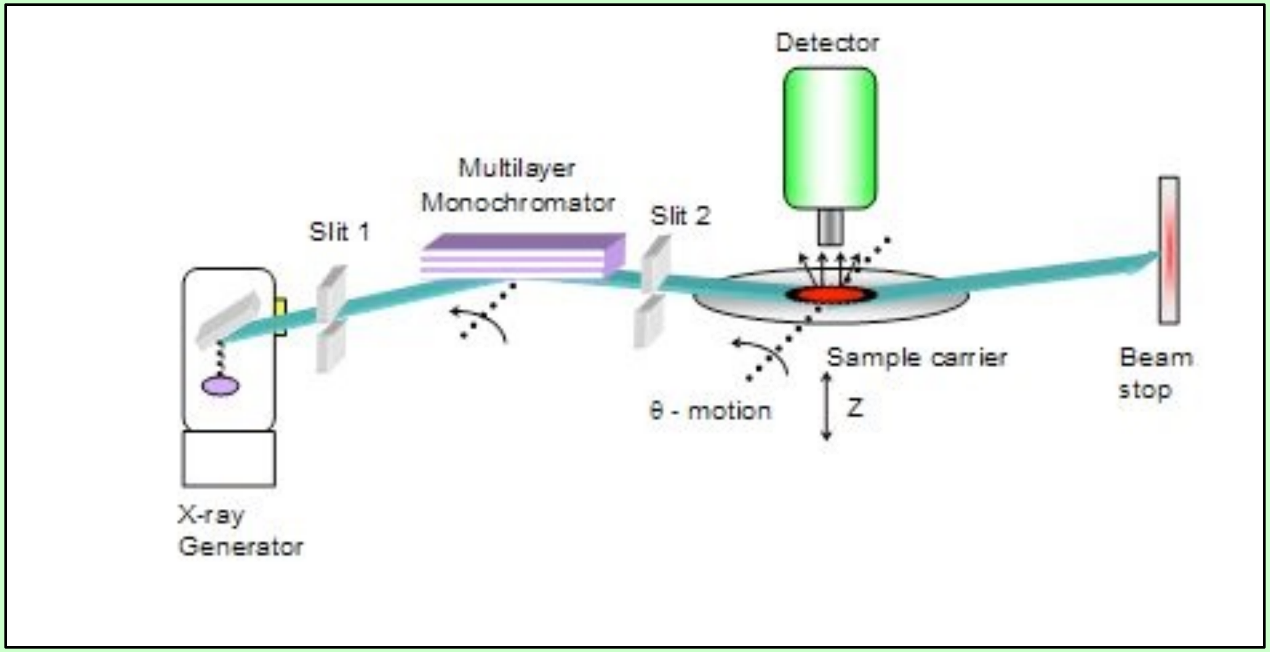
X-Ray Fluorescence



Total-reflection X-Ray Fluorescence



Components of a TXRF spectrometer



- X-ray tube
- Monochromator
- Sample carrier, adjustment
- Detector

Sample preparation



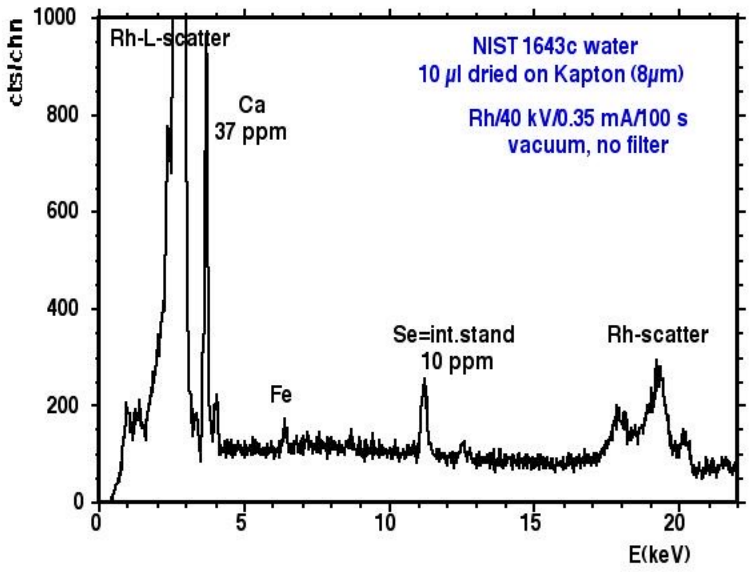

- fill sample in micro tube
- add internal standard
- homogenize
- pipette on carrier

https://www.bruker.com/en/landingpages/bna/how-does-TXRF-work.html

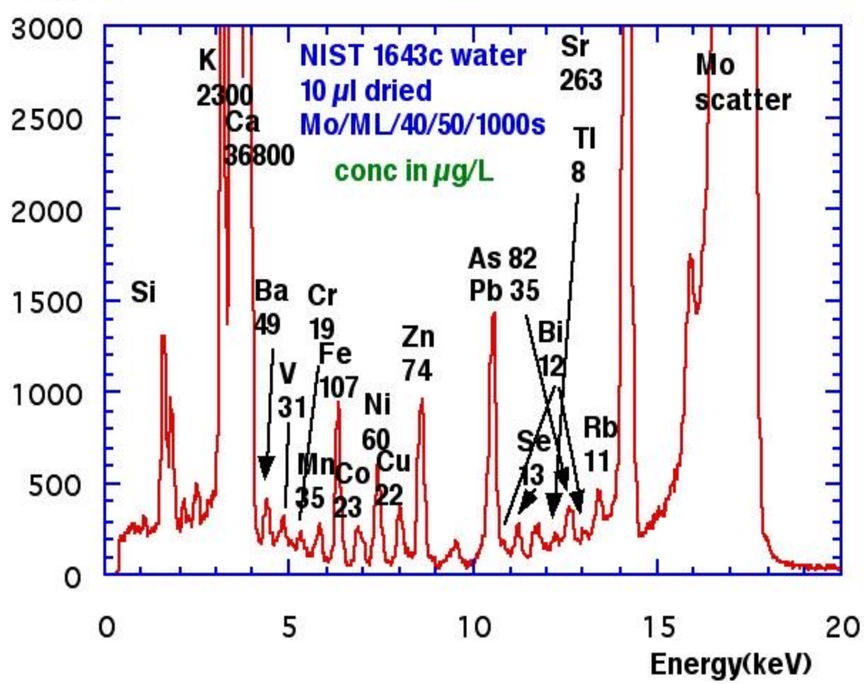
Standard XRF ⇔ TXRF

Fig. 6.2.1 Nist-TN500

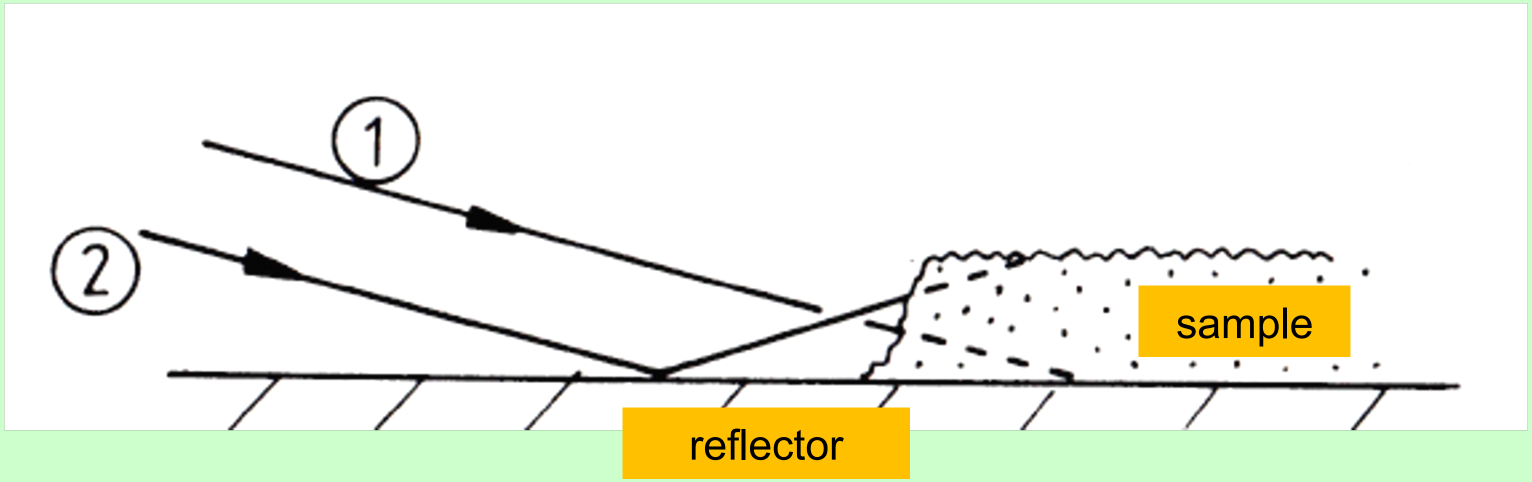
Standard EDXRF spectrometer TN5000



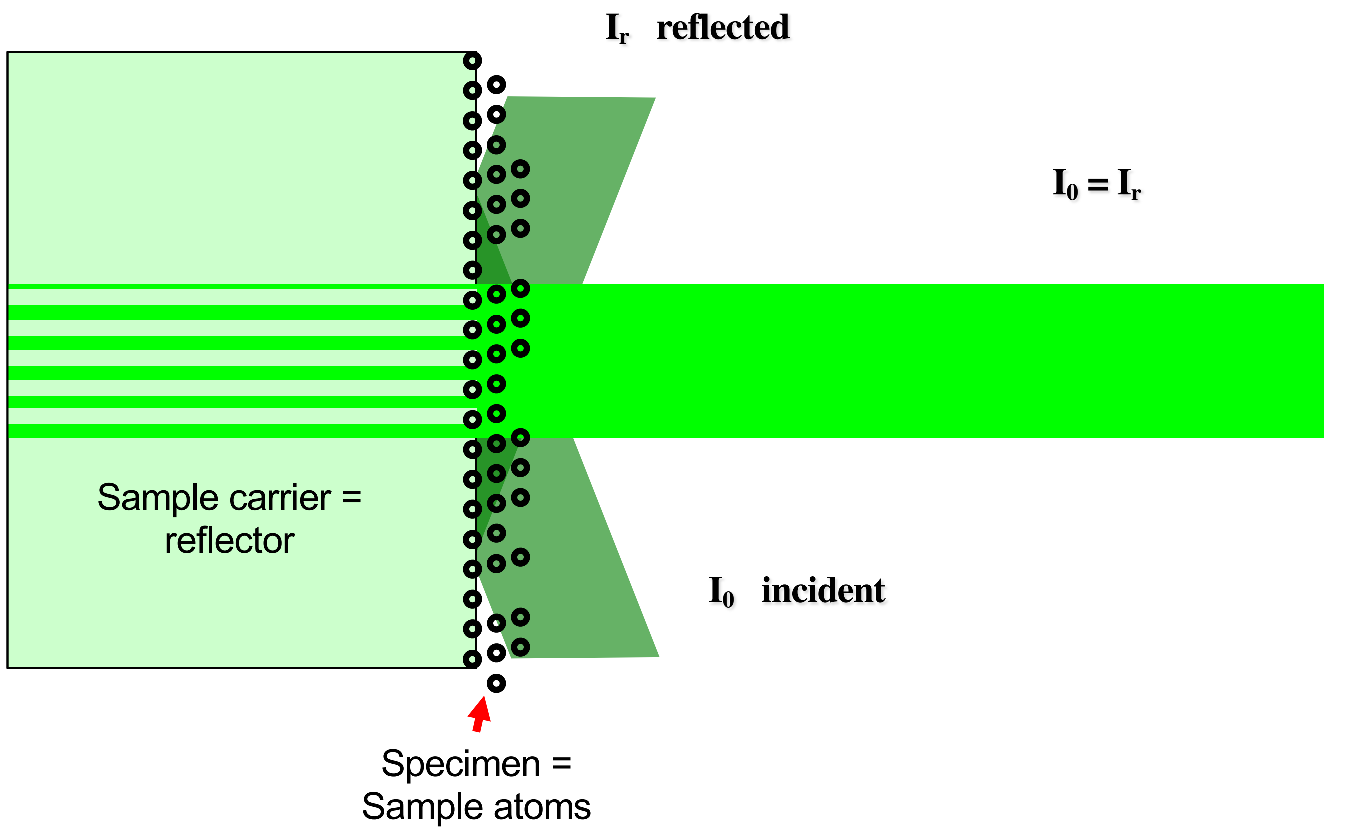
ATI- TXRF spectrometer



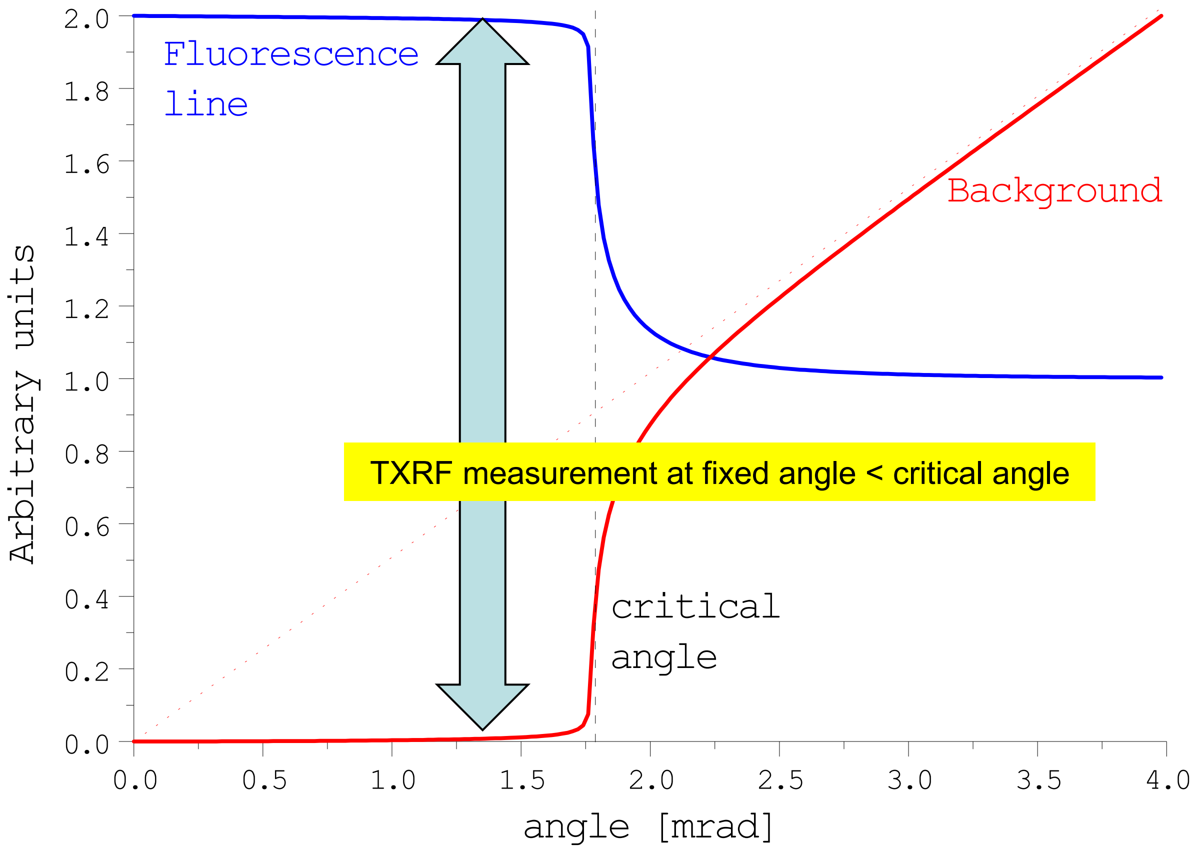
Double excitation



Less interaction with substrate (reflector)



TXRF basics



Line intensity

$I_L \propto (1 + R)$

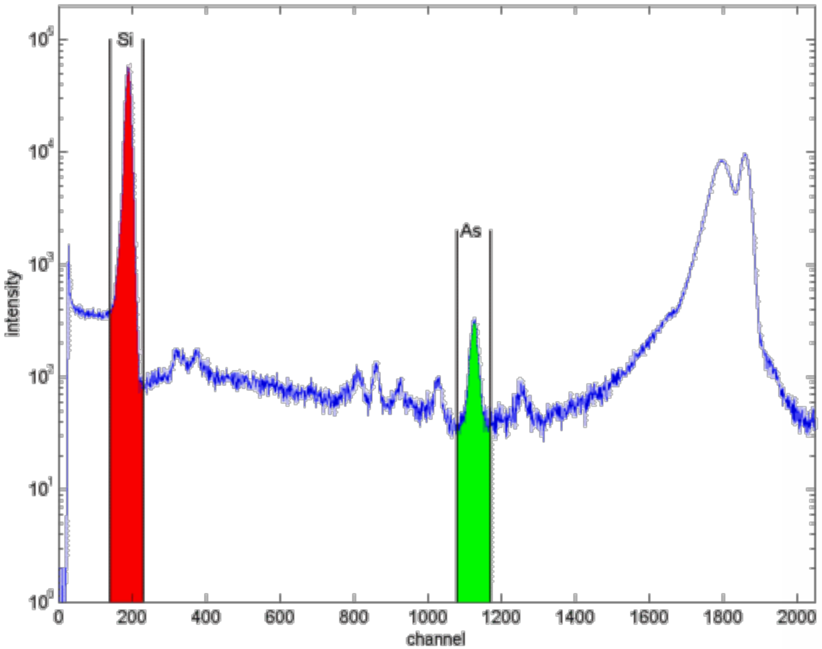
Background

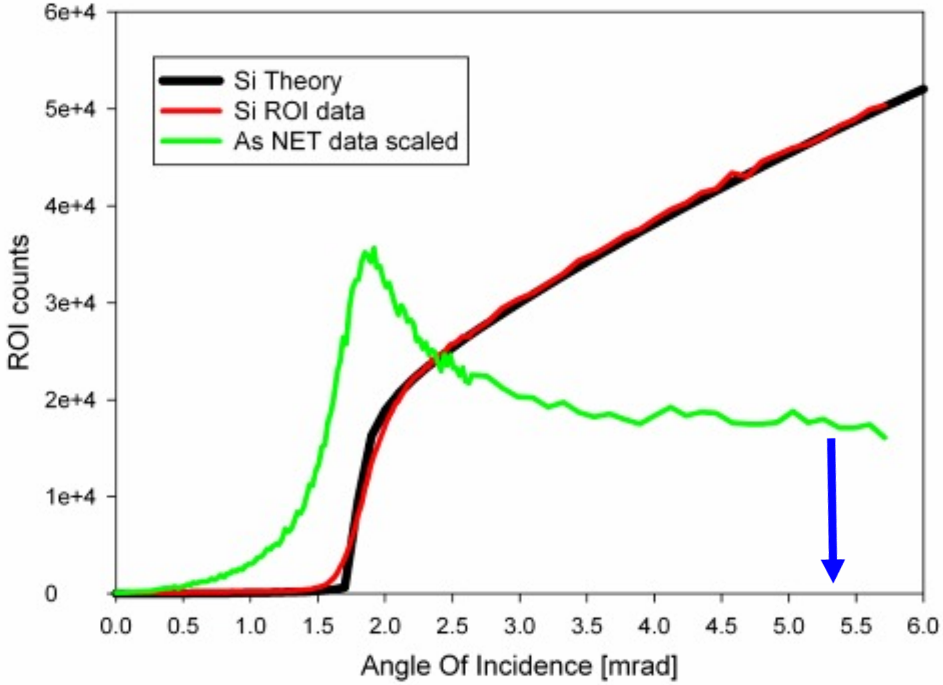
$I_B \propto (1 - R) \cdot \sin\phi$

Quartz reflector, Mo-Kα radiation

Intensity of an arsenic sample on a quartz reflector

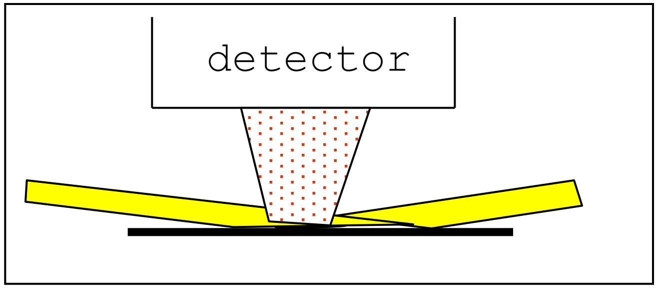
as function of the angle of incidence





by: F. Meirer

Advantages of TXRF



- background reduction
- double excitation of sample by both the primary and the reflected beam
- very short distance sample - detector (~3mm): large solid angle

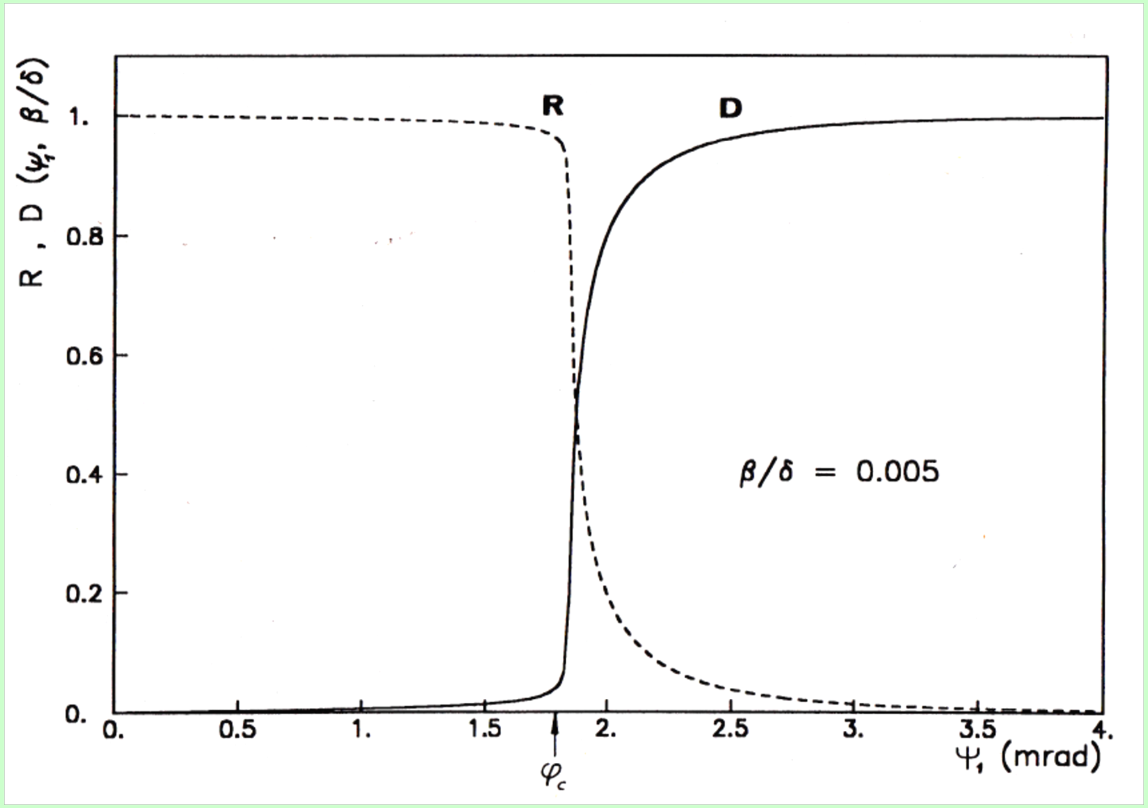
Analytical features:

- small sample amounts required (ng, some µl)
- detection limits in the pg (ppb) range with X-ray tube excitation
- simple quantification (thin film approximation) by adding an internal standard
- angle dependence of fluorescence signal : particle – film - implants

Total Reflection

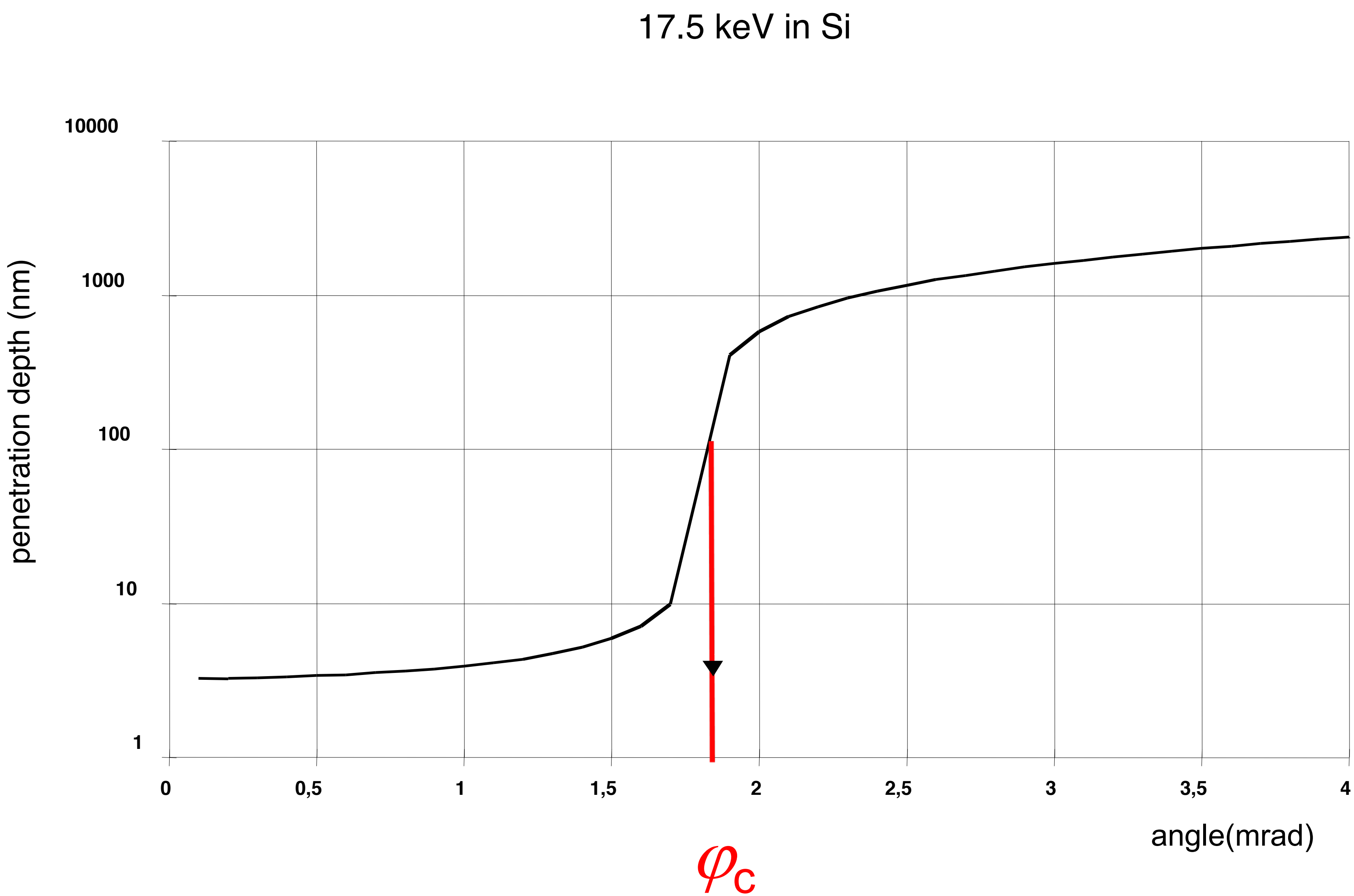
- 3 important quantities characterize total reflection:
  - The reflectivity *R*, which increases to almost 100% below the critical angle θ_c
  - The penetration depth, which is of only a few nanometers thickness
  - A standing wave field (interference zone)

Reflection ⇔ Transmission

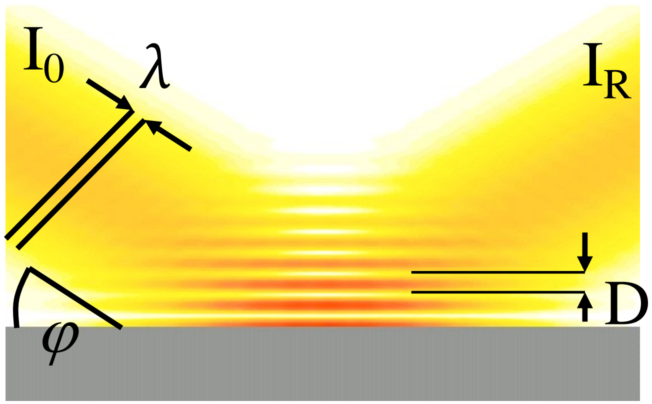


1 mrad => angle of 3.4 min => 0.057 degrees

Penetration depth (nm)



Standing wave



$$D = \frac{\lambda}{2 \cdot \sin \varphi}$$ (nm range)

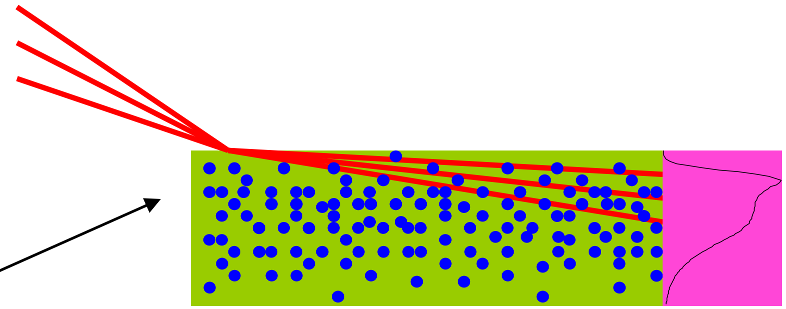
Distance *D* between nodes and antinodes is a function of the incident angle.

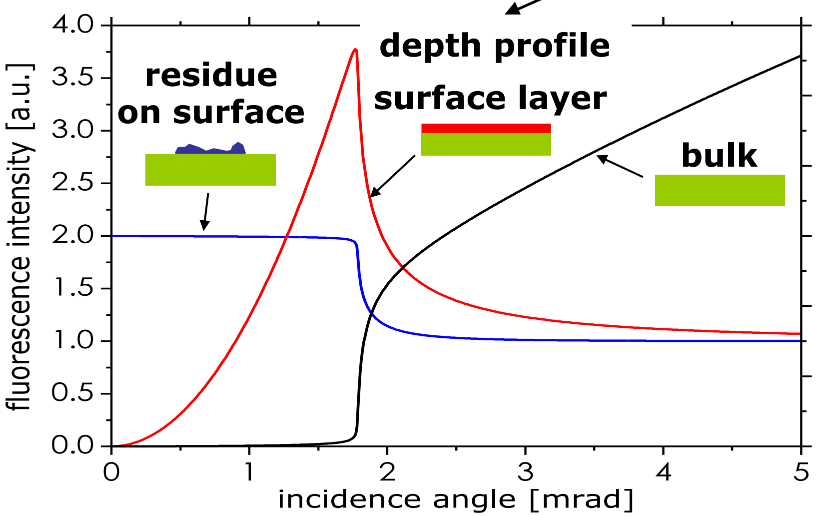
Inside the medium, the intensity decreases exponentially as a function of the refraction angle. => penetration depth x_p

Angle dependent signals

Angle dependence fluorescence signal ⇨ information sample type:

- bulk
- particle (residue on surface)
- film (surface layer)
- implants (depth profile)





The incident angle dependence of the fluorescence intensity gives information on the depth distribution of the element.

Thin-film approximation valid, if ...

A minute flat sample on the sample-carrier is practically an ideal sample:

- No sample self absorption correction
- No inter-element effect

Absolute Sensitivity

Ideally, there is a linear relationship between the recorded X-ray intensity I_i and the concentration c_i (or mass) of an analyte:

$$I_i = S_{\mathrm{abs}} \cdot c_i$$

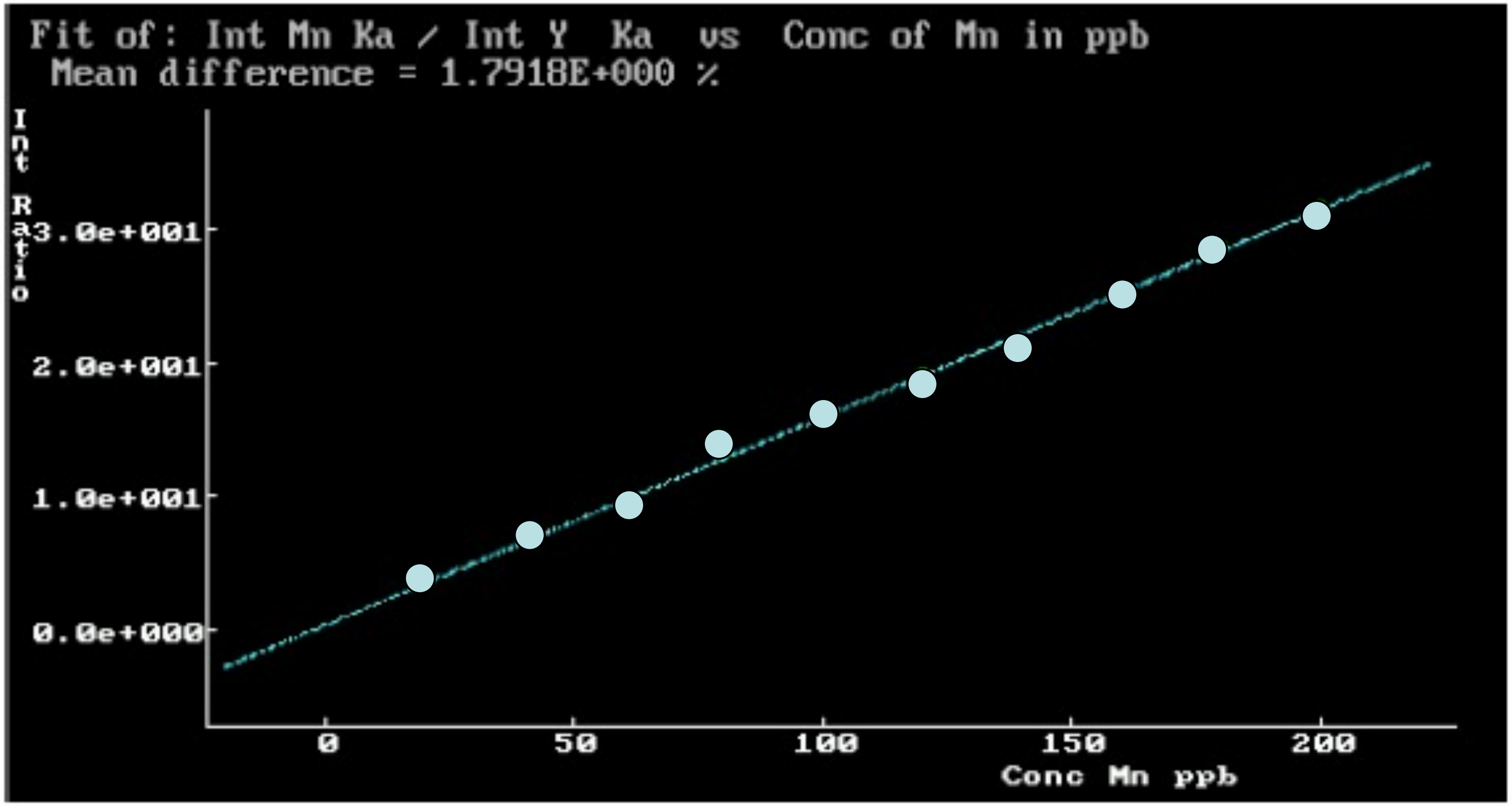
I_i	net intensity of the element *i*
S_{abs}	absolute sensitivity
c_i	concentration of *i*

TXRF quantification: Internal standard

Generally, the internal standard method is used for quantification. The same element used as internal standard is used as reference element.

The internal standard is an element initially not present in the sample. Typically, e.g. Ga, Y, or Co for acidic solutions, Ge for basic solutions.

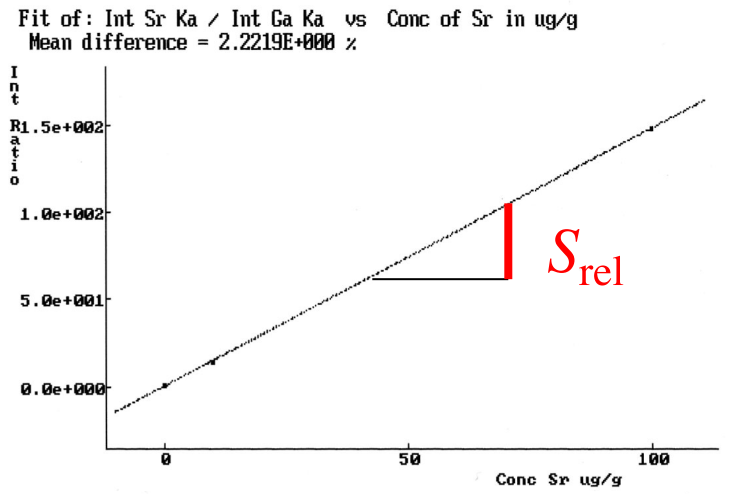
Calibration line for Mn, Internal standard: Y



Relative Sensitivities

The ratios of absolute sensitivities with reference to a specific element (internal standard) are called relative sensitivities and can be determined by calibration.

Calibration curve

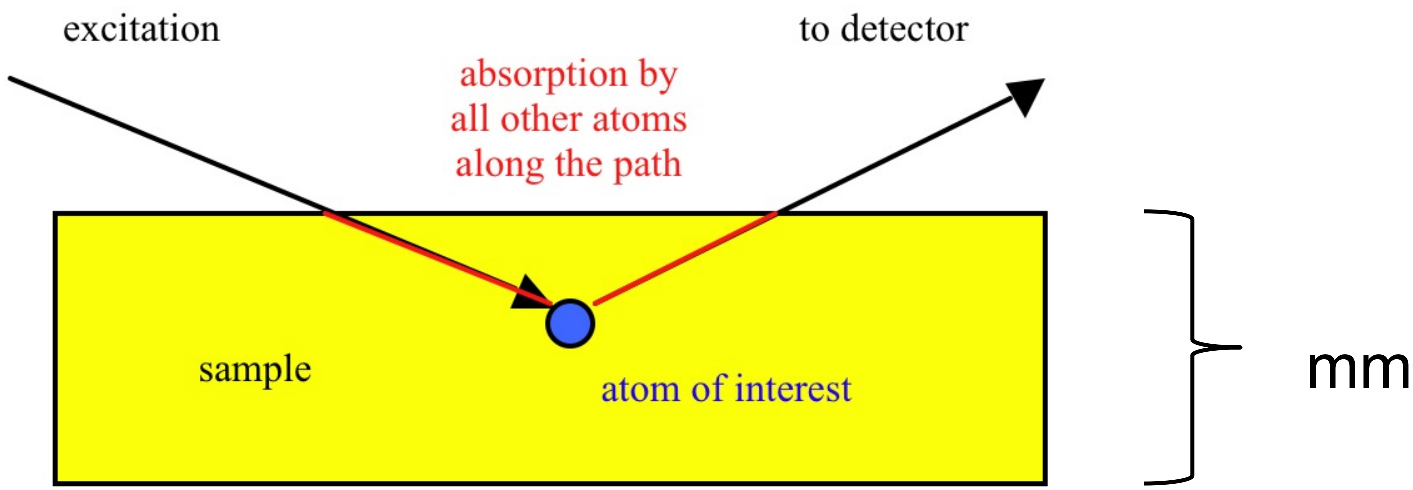


Quantification of unknown sample

$$c^i = \frac{I^i}{I^s} \cdot \frac{1}{S^i_{rel}} \cdot c^s$$

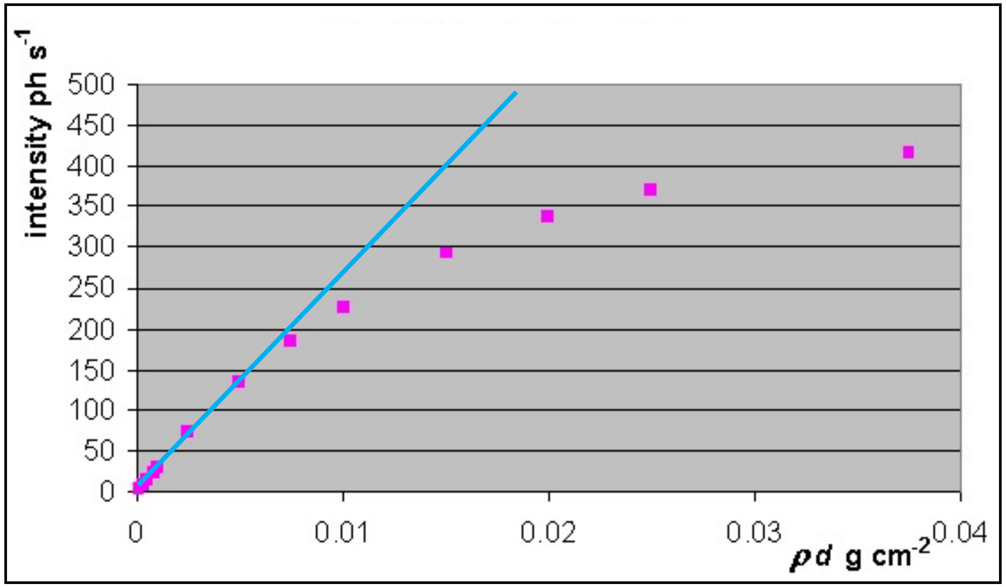
Standard XRF - Quantification

Greatest "handicap" for Quantitative XRF: Sample Self-Absorption

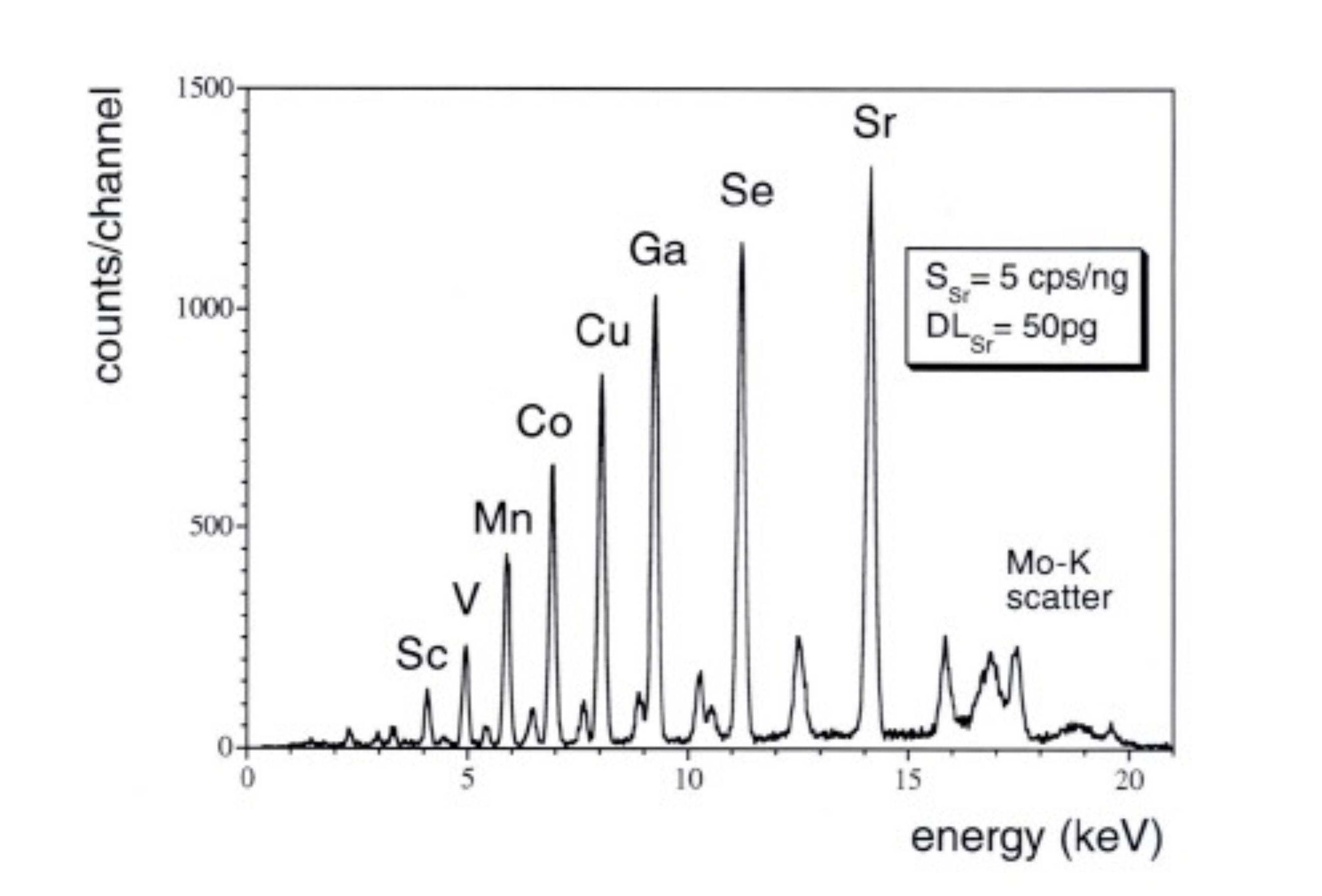


Both the exciting radiation and the fluorescence radiation of an atom (element) of interest
suffer from sample self-absorption.

How to be sure that our sample is thin?

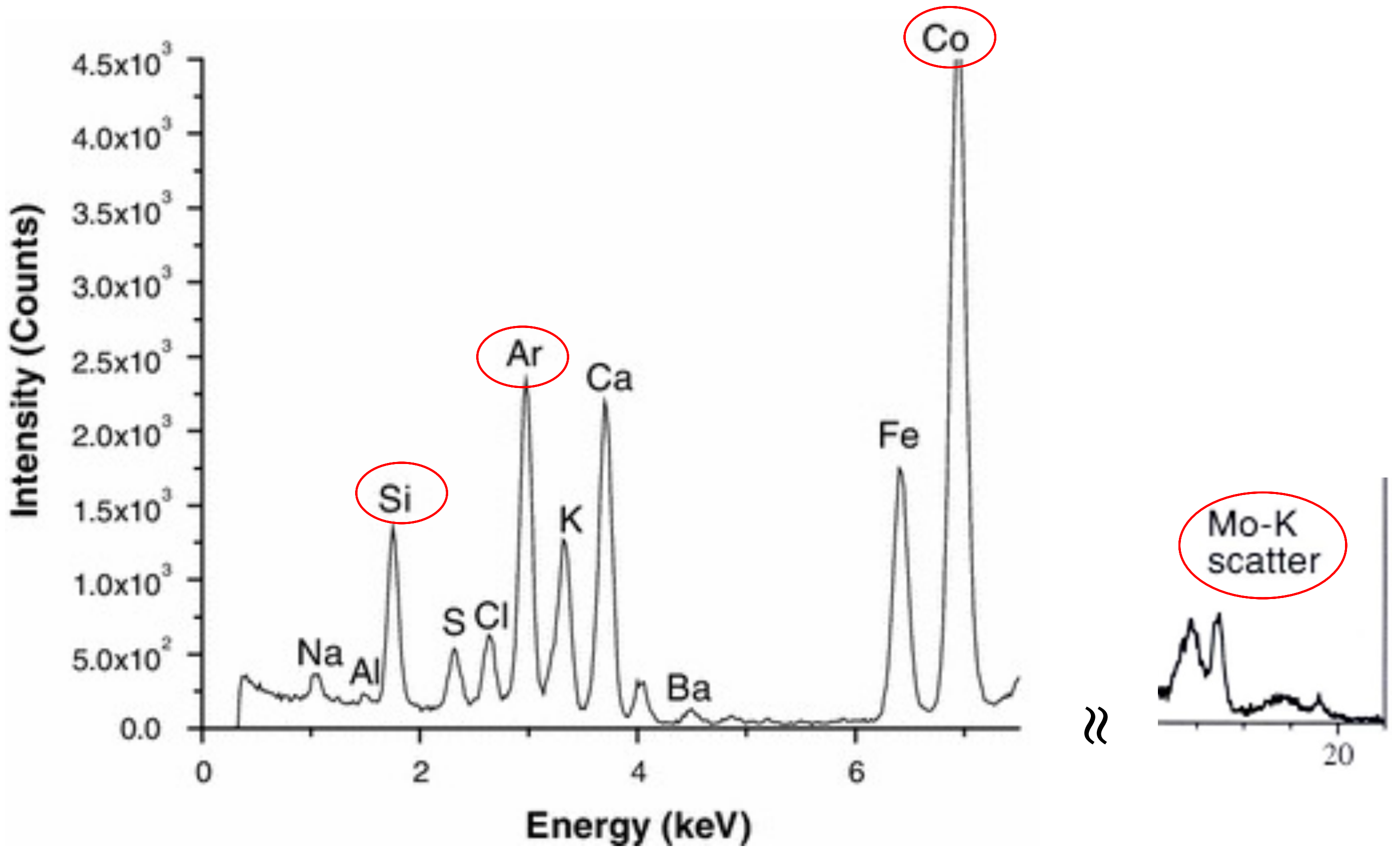


We add successive amounts to prepare synthetic samples and observe the growth in signal intensity for the elements of interest.



A typical spectrum of a calibration standard for TXRF analysis. All specified elements are present with equal amounts. Internal standard element: gallium

Si, Ar, Internal standard, scatter peaks

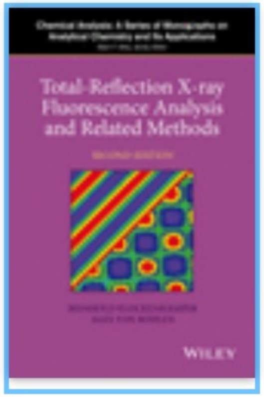


Misra, N.L. Characterization of nuclear materials by total reflection X-ray fluorescence spectrometry.
J Radioanal Nucl Chem **300,** 137–145 (2014). https://doi.org/10.1007/s10967-014-2972-x

Highlights of TXRF

- TXRF is a rather universal and economical method of multi-elemental analysis.
- Mainly liquid samples
- It is a micro-analytical tool for small samples or minute specimens.
- It is being effectively applied to trace element analysis.
- Detection limits can be in the pg/ml (ppb) range.
- An internal standard element has to be added. Simple quantification (as compared to standard XRF), since matrix effects are absent.

Recommended



Total-Reflection X-Ray Fluorescence Analysis and Related Methods

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Short and crispy:

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