Total Reflection X-ray Fluorescence Analysis.

This learning module is aimed to introduce you to the fundamentals of TXRF, as well as to the main specific features of this x-ray fluorescence technique.

Section 1

1. Introduction

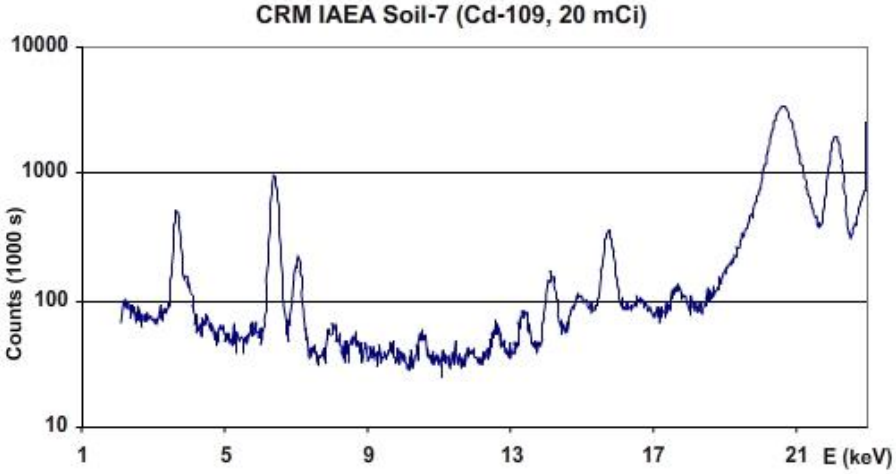
Total reflection X-rays fluorescence (TXRF) is a surface elemental analysis technique often used for the ultra-trace analysis of particles, residues, and impurities on smooth surfaces.

TXRF is essentially an energy dispersive XRF technique arranged in a special geometry. An incident beam impinges upon a polished flat sample carrier at angles below the critical angle of external Total reflection for X-rays, resulting in the reflection of most of the excitation beam photons at this surface. The sample, which is a small residue deposited in the sample carrier, is seen as a very thin sample under a very small angle. Due to this configuration, the measured spectral background in TXRF is less than in conventional XRF. This reduction results in increased signal to noise ratio.

TXRF can be classified according to its application scope:

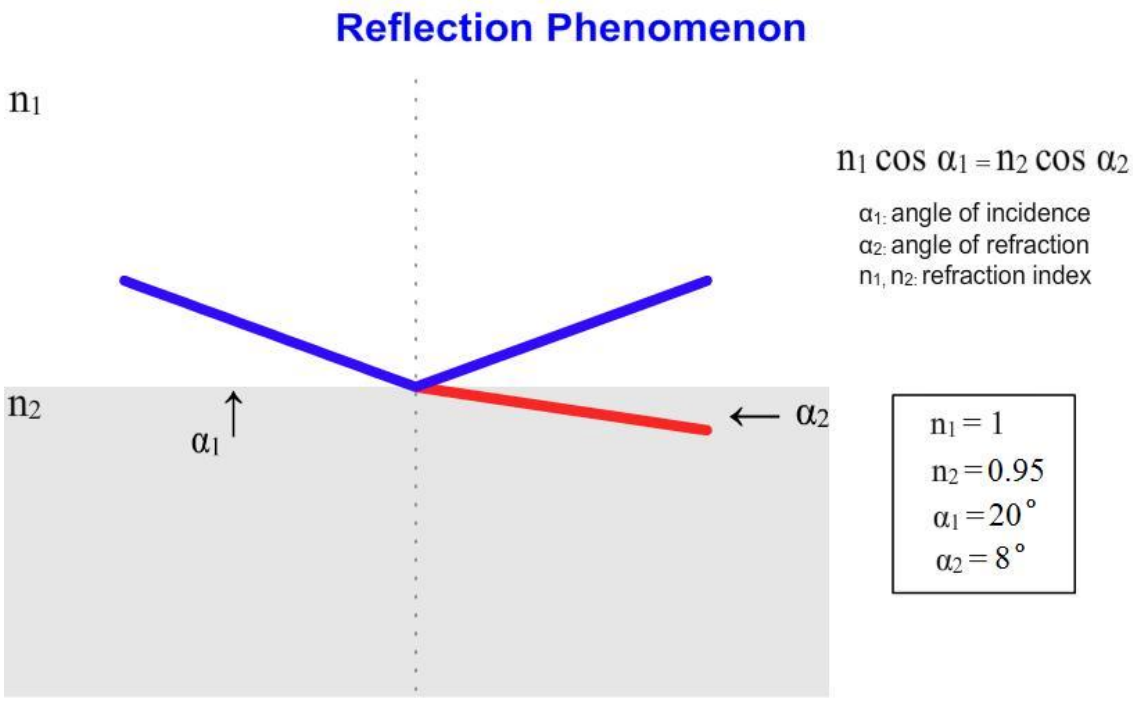
- **Bulk chemical analysis:** Samples are subjected to more or less intense processes of chemical treatment for suspension, dissolution, mineralization, pre-concentration and separation.
- **Micro analysis:** Minute amounts of sample (usually few grains) are analyzed. In this aspect TXRF is a valuable tool in archaeometry and forensics.
- **Surface analysis:** The chemical quality of flat surfaces is ready analyzed by TXRF.

One of the causes limiting the signal to noise ratio in EDXRF techniques based in the use of direct X-ray tube excitation is the presence of a significant background contribution in the measured spectra. This background is due to the scatter of the x-ray tube Bremstrahlung. Scattered high energy photons not only increase the background in the high energy region of the measured spectra, but also can undertake multiple scatter acts and appear as background in the low energy region.



1.1- Reflection phenomenon

X-rays, like any other electromagnetic wave, follow a straight line path in any homogeneous (transparent) medium, for example in vacuum. However, 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. The nature of the deflection depends on the energy of the photons, the properties of the media that form the interface and the angle of the beam. Under certain conditions, the beam can be even split, that is part of it is, partially reflected back to the first medium and partially refracted into the second one.



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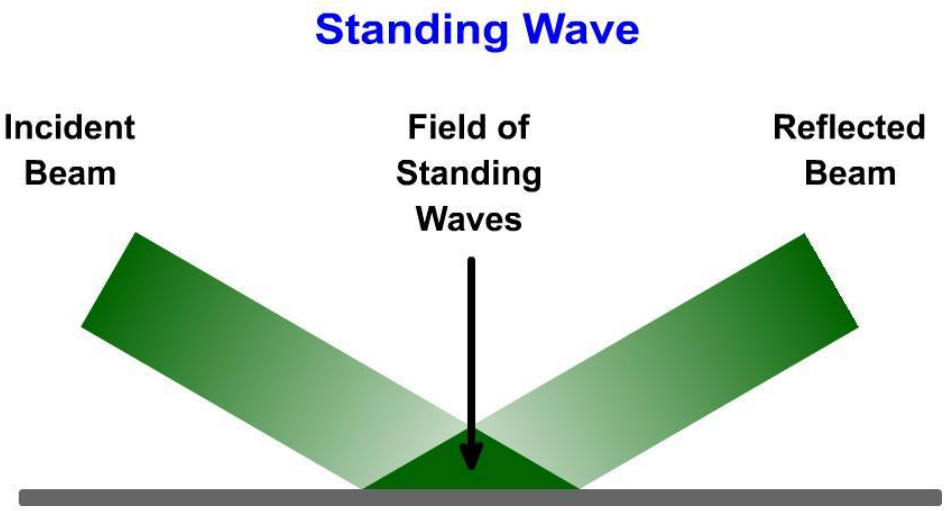
1.1.1- Total reflection phenomenon

Contrary to the behavior of the visible light photons, for X-rays any medium is less dense than vacuum and any solid is optically less dense than air. This results in a refracted beam deflected toward the interface. Following this logic, one can see that there is a minimum critical angle $\alpha_1 = \alpha_{crit}$ for which refraction is just possible. For angles α_1 smaller than α_{crit} no beam enters the medium 2. The interface behaves like an ideal mirror and completely reflects the incident beam back into the medium 1. This phenomenon is called **Total Reflection.**



1.1.2- Critical angle in total reflection

The critical angle can be calculated according to the following equation:

$$\alpha_{crit} \approx \frac{1.65}{E}\sqrt{\frac{Z}{A}\rho}$$

E= Photons energy in keV
Z= Atomic Number of the reflector
A= Atomic mass in g/mol
ρ= density in g/cm3

The values of α_{crit} laid between ~0.04° for Plexiglas at 35 keV, to ~0.55° for Gold at 8.4 keV (W-Lα). For Fused Quartz α_{crit} is 0.10° at 17.44 keV (Mo-Kα).

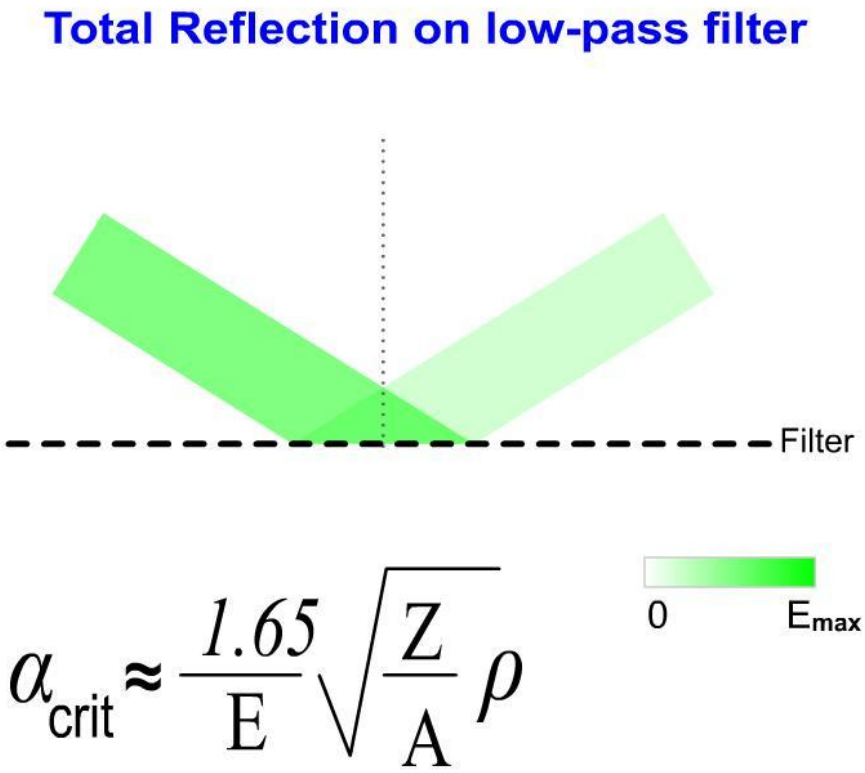
From the above equation two important conclusions can be made:

- A given energy photons are reflected only below a certain glancing angle called Critical Angle.
- A reflector set on a particular angle will reflect only certain photons out of a polychromatic beam, namely, those the energy of which fulfills the Total Reflection condition.

1.1.3- Total reflection on low-pass filter

Since Total Reflection angle depends on the energy of the photon, one can use this effect to modify the excitation spectrum beam. By eliminating the high energy photons from the excitation spectrum, it is possible to minimize their contribution to the background in the measured spectra, thus making possible to achieve better detection limits.

In this way it is possible to use the total reflection to "filter out" of a white polychromatic X-rays beam photons with energies above certain selected value. In other words, it is possible to use a flat substrate as a low-pass filter on X-rays, without substantially affecting the intensity of the beam.



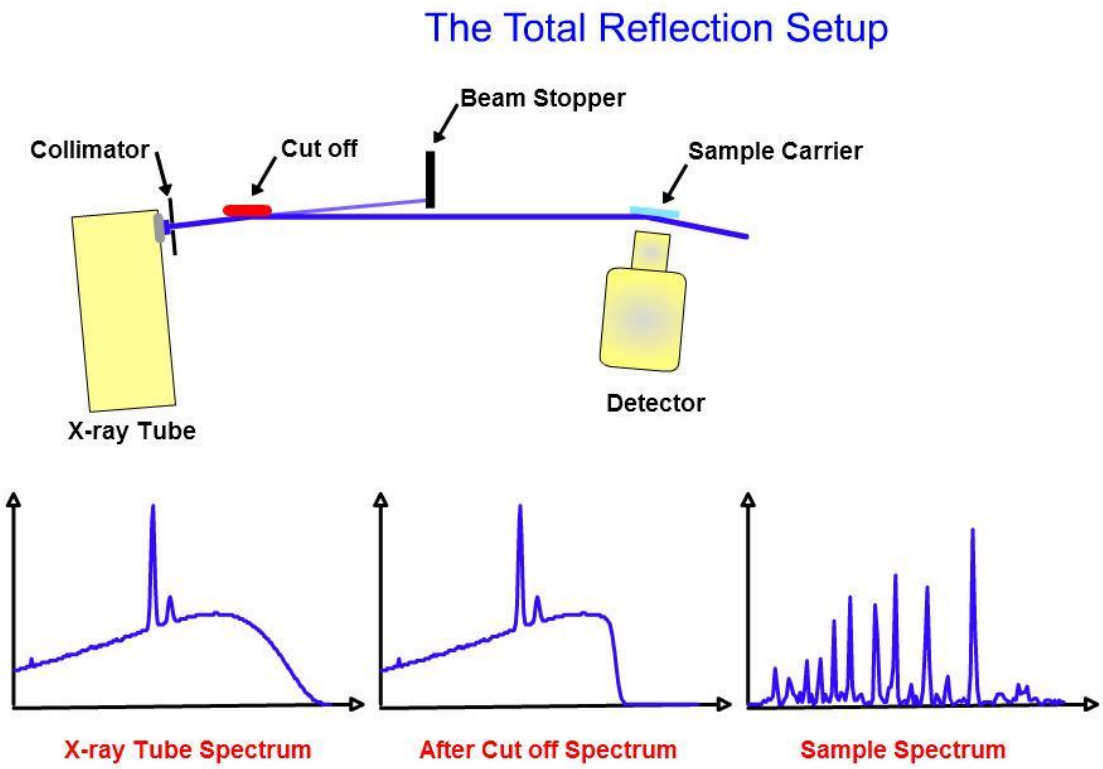
1.2- Basic TXRF Setup

There are several designs of TXRF spectrometers, but for general laboratory use they are normally based on the utilization of X-ray tubes. The polychromatic collimated beam of a conventional X-rays tube is deflected by the first reflector, which alters the primary spectrum. For most applications, a quartz flat polished glass block is sufficient, acting as a low pass filter for the removal of the high energy photons of the bremsstrahlung continuum (cut off). Alternatively this first reflector can be substituted by a device acting as monochromator. Some single crystals or multilayer structured devices are used, acting as Bragg reflectors.

Only the reflected beam at this spectrum modifier is allowed to hit the sample carrier under grazing incidence at an angle lower than that ensuring total reflection of the main excitation energy. The sample holder may be loaded with some sample material or may be the actual object of analysis itself.

The x-ray radiation emerging from the sample is measured using an energy dispersive solid sate detector, usually a Si(Li) detector. Since scatter cross sections are minimal at 90 degrees, the detector is mounted with its entry window parallel to the sample carrier plane, in order to obtain spectra with the minimum scattered background. The distance to the sample is reduced to about 1 mm in order to secure the detection of the fluorescence radiation within a large solid angle. The measured signal is sorted by amplitude (proportional to the energy of the x-rays) in a multi-channel analyzer, leading to an energy dispersive spectrum. Measurements can be carried out in air ambient, but more sophisticated sample chamber can be designed as to perform measurements under vacuum or helium flush to reduce attenuation of the low energy characteristic emission radiation in the air.

1.2.1- TXRF Setup representation



1.3- TXRF for trace analysis purposes

TXRF is a rather versatile and cost-effective method for multi-elemental analysis.

- It can be used as micro-analytical tool for minute specimens, such as small grains deposited in the sample carrier.
- It has been effectively applied to element trace analysis in various fields of research.
- Due to the improvement in signal to noise ratio, the instrumental detection limits are typically in the range of pg or ng/mL.
- As the sample constitutes a very thin layer, the quantification is less prone to matrix influence (no need for correction of attenuation or enhancement effects).