Total Reflection X-Ray Fluorescence Spectroscopy using the PicoTAX - Working principles

Main principle
The main principle of X-Ray Fluorescence Spectroscopy (XRF) is based on the fact, that atoms, when irradiated with X-Rays, radiate secondary X-Rays – the Fluorescence radiation. On this basis XRF-analysis is possible because:

- The wavelength and energy of the Fluorescence radiation is specific for each element.
- The concentration of each element can be calculated using the intensity of the Fluorescence radiation.

TXRF analysis using the PicoTAX
The working principle of Total reflection X-Ray Fluorescence spectroscopy as realized in the PicoTAX spectrometer is shown in Figure 1.

The X-Ray beam, generated by the Molybdenum-tube, is reflected on a Ni/C-multilayer resulting in a monochromatic X-Ray beam. This small beam passes the sample holder carrying the sample at a very small angle (0.3 – 0.6 °) causing total reflection of the beam. The characteristic Fluorescence radiation emitted by the sample is detected by an energy-dispersive detector (XFlash® detector) and the intensity is measured by means of an amplifier coupled to a multi-channel analyzer.

The main difference with respect to common XRF-spectrometers is the use of monochromatic radiation and the total reflection optic. Illuminating the sample with a totally reflected beam reduces the absorption as well as the scattering of the beam in the sample and its matrix. Resulting benefits are a largely reduced background noise, and consequently much higher sensitivities and the significantly reduction of matrix effects. One major advantage of TXRF, compared to atomic spectroscopy methods like AAS or ICP-OES, is the avoidance of memory effects.

The technical parameters of the PicoTAX spectrometer are summarized in Table 1.

Sample types and preparation
A summary of samples types, which can be analyzed by means of TXRF is given in Table 1, showing the great variety of applications. For TXRF analysis all samples must be prepared on a sample tray, which reflects X-Ray radiation. For this purpose the usage of trays with a diameter of 30 mm, made of acrylic or quartz glass is common. Liquids can be prepared directly on the sample tray. An amount of several µl is transferred to the glass disc using a pipette and subsequently evaporated in a desiccator or drying oven (Figure 3.). For solid samples different kinds of preparation are possible.

Powdered samples (suspended matter, soils, minerals, metals, pigments, biogenous solids etc.) can be analyzed directly after preparation of the material on the sample tray. Typically, a few µg of sample material are transferred, using a Q-tip or a lint-free tissue. In a similar way the direct preparation of single microsamples (particles, slivers etc.) is possible.
Alternatively, powdered solids can be prepared as a suspension with volatile solvents like acetone or methanol. The suspension is then pipetted onto the sample tray.

In Figure 3 the sample preparation is described for solids, which were digested by microwave digestion.

**Analysis and quantification**

In general all elements starting from Sodium up to Uranium (excl. Niobium, Molybdenum and Technetium) can be analyzed by the PicoTAX (Figure 4.). TXRF analysis is based on internal standardization. Therefore, an element, which is not present in the sample, must be added for quantification (Figure 3).

The complete process of analysis and quantification is described by the following steps:

- **Measurement** of the complete spectrum.
  - All detectable elements are measured simultaneously.
- **Evaluation** of the measured spectra
  - All identified elements have to be marked for further quantification, which can be done manually or automatically by the software.
- **Spectra deconvolution**
  - On the basis of the chosen elements, the software performs the deconvolution of the spectra. The net intensities of the element peaks are calculated with regard to corrections of line overlaps, background factors, escape peak correction etc.
- **Calculation of concentrations**
  - The element concentration is calculated by the simple formula:
    \[
    c_x = \frac{N_x S_x c_x}{S_{is}}
    \]
  - where \(N\) is the net intensity, \(S\) the relative sensitivity and \(c\) the concentration - each either of the analyte \(x\) or the internal standard \(is\), as indicated.

The typical detection limits of the PicoTAX in aqueous solutions is presented in Figure 5.

**Summary**

The PicoTAX TXRF spectrometer is a versatile instrument for trace element analysis of different kinds of samples. It is completely independent of any cooling media and therefore applicable for on-site analysis. Further benefits of the PicoTAX are the simple calibration routine, the absence of matrix or memory effects and the ability for fast multi-element analysis.

**Literature**