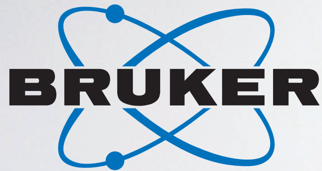


TXRF

Total Reflection X-ray Fluorescence Spectroscopy - Working Principles

Application Note # XRF 426

Main principle

The main principle of X-ray Fluorescence Spectroscopy (XRF) is that atoms, when irradiated with X-rays, emit 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 S2 PICOFOX

The working principle of Total Reflection X-ray Fluorescence (TXRF) spectroscopy as realized in the S2 PICOFOX spectrometer is shown in Figure 1.

The X-ray beam, generated by the Molybdenum tube, is reflected on a multilayer monochromator resulting in a monochromatic X-ray beam. This small beam impinges on the sample holder carrying the sample at a very small angle (< 0.1°) causing total reflection of the beam. The characteristic fluorescence radiation emitted by the sample is detected by an energy-dispersive detector and the intensity is measured by means of an amplifier coupled to a multichannel analyzer.

The main difference with respect to common XRF spectrometers is the use of monochromatic radiation and the total reflection optics. Illuminating the sample with a totally reflected beam reduces the absorption as well as the scattering of the beam in the sample matrix. Resulting benefits are a greatly reduced background noise, and consequently much higher sensitivities and a significant reduction of matrix effects.

Another 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 S2 PICOFOX spectrometer are summarized in Table 1.

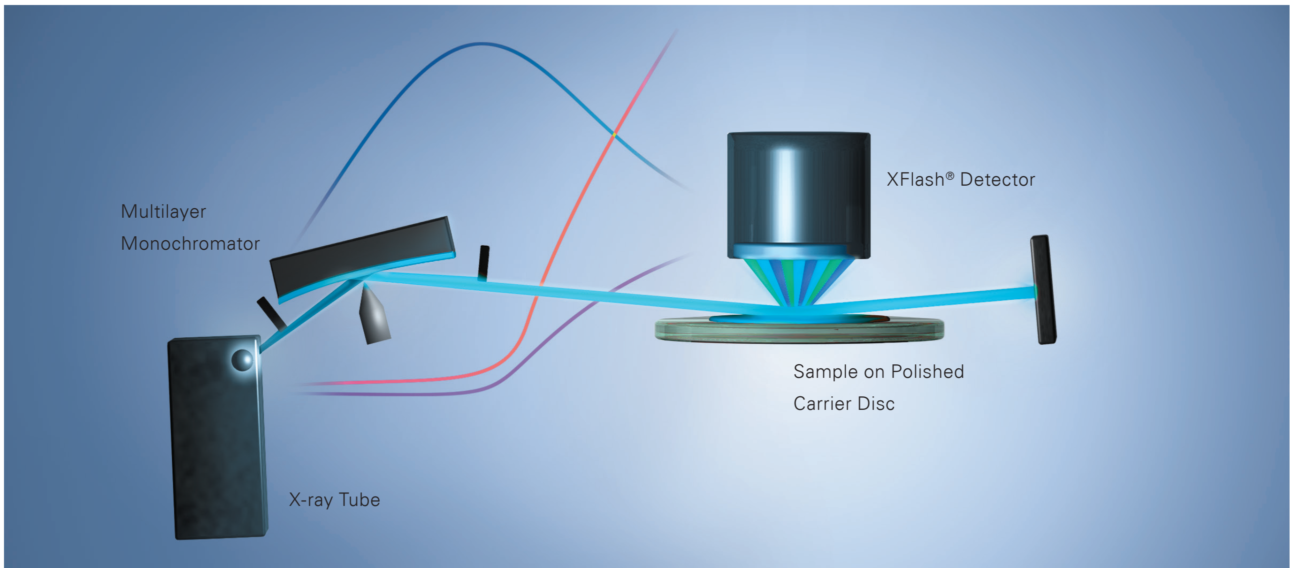


Figure 1
Schematic working principle of the S2 PICOFOX spectrometer

Sample types and preparation

A summary of sample types that can be analyzed by means of TXRF is given in Table 2 show the large variety of applications. For TXRF analysis all samples must be prepared on a sample tray that reflects X-radiation. For this purpose the usage of trays with a diameter of 30 mm made of acrylic or quartz glass is common.

Liquids and microwave digested solid samples 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 cotton bud 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.

Table 1
Technical parameters of the TXRF spectrometer S2 PICOFOX

Parameter	Specifications
X-ray tube	Air-cooled metal ceramic Mo or W anode, max. power 30 or 40 W
Optics	Multilayer monochromator (17.5 keV)
Detector	Si drift detector XFlash® Area: 30 mm², FWHM: < 150 eV (Mn Kα)
Size (DxWxH)	450 x 590 x 300 mm
Weight	37 kg

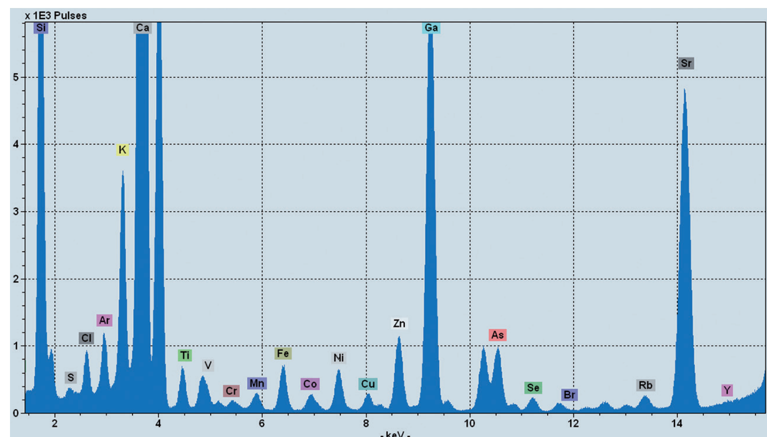


Figure 2
Typical energy-dispersive spectrum of a TXRF spectrometer

Liquids and Suspensions	Solids (Inorganic)	Solids (Biogenous)
Water: potable, river, rain, sea and waste water	Thin layers: contaminations, films, foils, precipitates	Plant and wooden material: algae, leaves, braid, moss, needles, roots
Body fluids: blood, serum, urine	Pigments: creams, inks, oil paint, powder	Food: fish, fruits, meat, nuts, vegetables
Pure chemicals: acids, bases, solvents, water	Minerals: ores, rocks, silicates, silicon	
Suspended particles: aerosols, dusts, flue ash	Soil: mud, sediments, sewage sludge	Tissue: hair, kidney, liver, lung, nails
Oils: combustibles, crude oil, fat and grease	Metals: aluminum, iron, steel	

Table 2
Sample materials analyzable by TXRF (KLOCKENKÄMPER, 1997)

Analysis and quantification

In general all elements from sodium to uranium (excl. Niobium to Technetium) can be analyzed by the S2 PICOFOX (Figure 2). TXRF analysis is based on internal standardization. Therefore, an element, which is not present in the sample, must be added for quantification purposes (Figure 3).

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

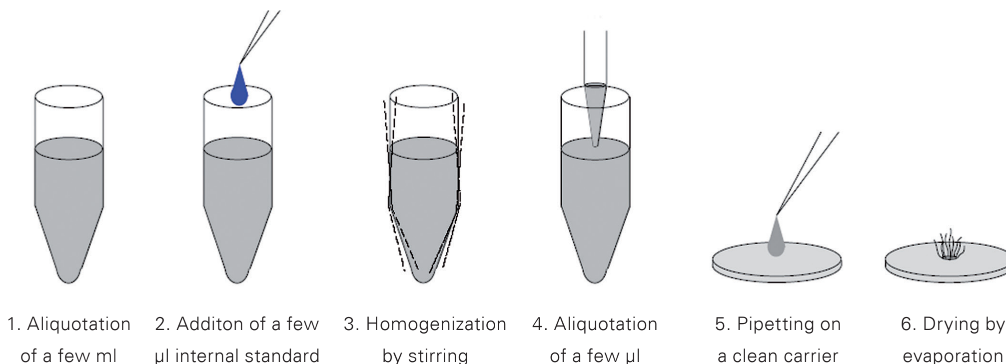
- **Measurement of the complete spectrum.** All detectable elements are measured simultaneously.
- **Evaluation of the measurement spectra.** All identified elements are be marked for further quantification, which can be done manually or automatically by the software.
- **Spectra deconvolution** On the 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:

$$c_x = \frac{N_x / S_x}{N_{is} / S_{is}} \cdot c_{is}$$

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.

As shown in Figure 4, the S2 PICOFOX can measure the elements Al to Y using spectral K-lines. Elements Ru to U are measured using L-lines.

The typical Limits of Detection (LODs) of the S2 PICOFOX are presented in Figure 5. The LOD for many elements is close to or below 1 µg/l.



1. Aliquotation of a few ml
2. Additon of a few µl internal standard
3. Homogenization by stirring
4. Aliquotation of a few µl
5. Pipetting on a clean carrier
6. Drying by evaporation

Figure 3
Sample preparation steps for the TXRF analysis of liquids

Summary

The S2 PICOFOX TXRF spectrometer is a versatile instrument for trace element analysis of different kinds of samples. It is completely independend of any cooling media and therefore applicable for on-site analysis. Further benefits of the S2 PICOFOX are the simple calibration routine, the absence of matrix or memory effects and the ability for fast multi-element analysis.

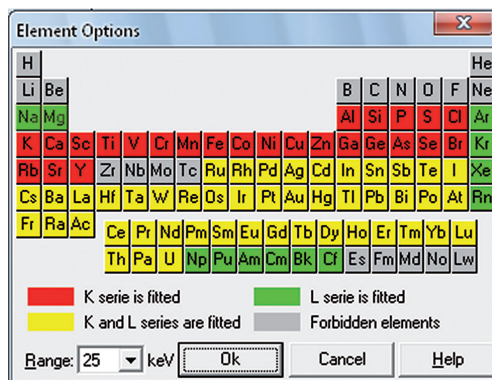


Figure 4
Overview of elements that can be measured by the S2 PICOFOX spectrometer

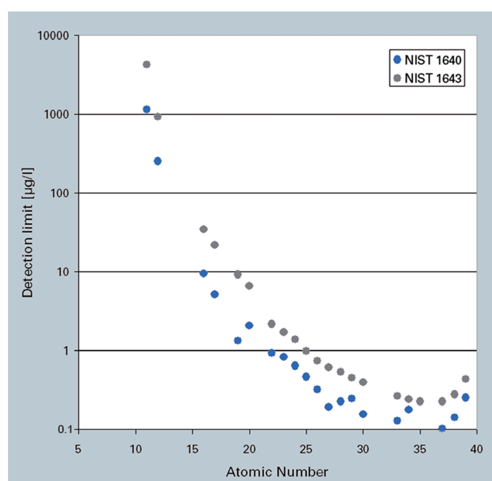


Figure 5
Limits of Detection of the S2 PICOFOX

Literature

Klockenkämper, R. (1997): Total-Reflection X-Ray Fluorescence Analysis, Wiley & Sons.

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