

## **Total Reflection X-Ray Fluorescence Spectroscopy -Working Principles**

**Ashok Kumar Gupta**

Assistant Professor & HOD - Mechanical Engineering,

Rishiraj Institute of Technology, Indore (M P) 453331

Email: [ashokgagorni@gmail.com](mailto:ashokgagorni@gmail.com)

### **Abstract:**

The total reflection X-ray fluorescence (TXRF) method has been used for the analysis of various types of solid materials of biological, geological and environmental origin. X-ray Fluorescence Spectroscopy (XRF) has reached the stage where it is classified as a mature analytical technique. The theoretical principles are well understood. In addition modern instrumentation demonstrates enhanced generator and temperature stability. High sensitivity is possible even for light elements and effective matrix correction software is available to the modern day spectroscopist. Apart from its continued applications in research and development, XRF has become a routine process control tool.

X-ray Powder diffraction (XRD), on the other hand, has with minor exceptions as in the cement industry, largely remained a research tool, despite being an older analytical technique than XRF. XRD has progressed significantly in the past decade from a mainly qualitative technique for the identification of crystalline materials to a quantitative tool with the advance of more powerful software packages. This software has improved instrument control, but also quantification and structure determination using the Rietveld method. Consequently, XRD is rapidly entering the process control environment.

This paper proposes the standardization of total reflection X-ray fluorescence (TXRF) analysis for environmental and biological samples. The importance of TXRF in environmental and biological analysis is now well established and it is continuously growing. However in these fields there are not standardized methods reported by the International Standard Organization (ISO). For this reason, the international collaboration for the development of new standard procedures and methods for TXRF analysis is required. Indeed, a project for “Inter laboratory comparison of TXRF spectroscopy for environmental analysis” was set up in the frame of the Versailles Project on Advanced Materials and Standards, with the aim of developing a new ISO standard for TXRF devoted to environmental and biological analysis.

Total Reflection X-ray Fluorescence (TXRF), an advanced variant of Energy Dispersive X-ray Fluorescence (EDXRF), is a comparatively new technique of material characterization. The geometrical improvements in TXRF lead to betterment of detection limits by several orders of magnitude compared to that of EDXRF. TXRF can be used mainly in three types of applications: trace element analysis, micro analysis and depth profiling.

**Key Words:** Total reflection X-ray fluorescence (TXRF), X-ray Powder diffraction (XRD), X-ray Fluorescence Spectroscopy (XRF), Sample Preparation

## **Introduction:**

### **X-ray Fluorescence Spectroscopy (XRF)**

XRF is a good general purpose analytical tool that can analyze both solid and liquid samples. It is based on the effect of the interaction of x-rays with matter, which causes excitation of certain electrons, which when relaxing to their ground state, emit x-rays of a characteristic wavelength for that element. This method, which can be non-destructive, is very good for identifying impurities in metals or characterizing a particular alloy. It may also be used for characterizing impurity levels of chemical compounds. Detection limits vary with the nature of the sample and the elements present but usually of the order of 0.1% by weight. For solid samples, this technique can only analyze the first few hundred

microns of the surface. For this reason, it is not suitable for inhomogeneous solid mixtures.

### **Total Reflection X-ray Fluorescence Spectroscopy (TRXRF)**

This method is similar to XRF except that the incident x-rays arrive at a very shallow angle to the substrate and do not penetrate it. Instead, characteristic radiation is produced by the very top layers of the sample including any contaminants. To be effective, the substrates should be flat and this has led to it being adopted for the identification of contaminants on semiconductor wafers. However, other samples may be examined providing they are sufficiently flat. Detection limits are dependant on the elements present but are in the ppb to ppm range.

### **X-ray diffraction**



### **From powders and solids to thin films and nanomaterials**

In materials research, the scientist has many analytical questions related to the crystalline constitution of material samples. XRD is the only laboratory technique that reveals structural information, such as chemical composition, crystal structure, crystallite size, strain, preferred orientation and layer thickness. Materials researchers therefore use XRD to analyze a wide range of materials, from powders and solids to thin films and nanomaterials.

## **Science and industry**

Many researchers, in industrial as well as in scientific laboratories, rely on X-ray diffraction as a tool to develop new materials or to improve production efficiency. Innovations in X-ray diffraction closely follow the research on new materials, such as in semiconductor technologies or pharmaceutical investigations. Industrial research is directed towards ever-increasing speed and efficiency of production processes. Fully automated X-ray diffraction analysis in mining and building materials production sites results in more cost-effective solutions for production control.

## **Solutions for analytical questions**

X-ray diffraction analysis meets many of the analytical needs of a materials scientist. In powders, chemical phases are identified qualitatively as well as quantitatively. High-resolution X-ray diffraction reveals the layer parameters such as composition, thickness, roughness and density in semiconductor thin films. Small-angle X-ray scattering and pair distribution function (PDF) analysis help to analyze the structural properties of nano materials. Stresses and preferred orientation can be determined in a wide range of solid objects and engineered components.

X-ray fluorescence (XRF) spectrometry is an elemental analysis technique with broad application in science and industry. XRF is based on the principle that individual atoms, when excited by an external energy source, emit X-ray photons of a characteristic energy or wavelength. By counting the number of photons of each energy emitted from a sample, the elements present may be identified and quantities.

Henry Moseley was perhaps the father of this technique, since he, building on W.C. Röntgen's discovery of the high-energy radiation dubbed X-rays, built an X-ray tube which he used to bombard samples with high-energy electrons. Moseley in 1912 discovered a mathematical relationship between the element's emitted X-ray frequency and its atomic number. In 1925 Coster and Nishina were the first to use primary X-rays instead of electrons to excite a sample. After Glocker and Schreiber were the first to perform quantitative analysis of materials using XRF in 1928, detector technology had to catch up in order to make the technique practical, which didn't begin to happen until the 1940's. The 1950's saw the first commercially produced X-ray spectrometers. In 1970, the lithium drifted silicon detector was developed, and this technology is still in use today (Jenkins 1988: 51-53).

Modern XRF instruments are capable of analyzing solid, liquid, and thin-film samples for both major and trace (ppm-level) components. The analysis is rapid and usually sample preparation is minimal or not required at all.

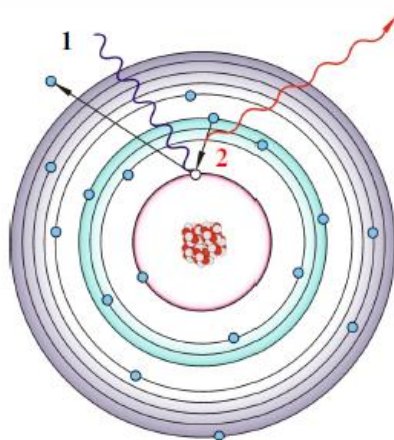
The Archaeometry Laboratory at the MU Research Reactor is the home of two Bruker Tracer III-V handheld instruments (one equipped with an automated sample changer) and an Elva-X benchtop instrument. These instruments are used primarily for the provenance research on obsidian artifacts from around the world, but they are also used in special circumstances for the non-destructive analysis of other materials such as metals, ceramic paints, and soils.

### **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.



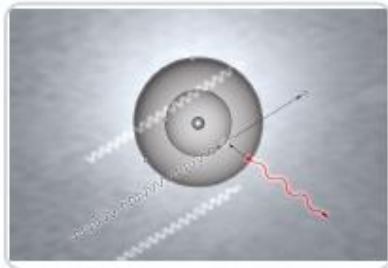
- 3 1. An X-ray quantum hits an inner shell electron in a (sample) atom. The electron is removed leaving the atom in an excited state
2. The missing inner shell electron is replaced by an electron from an outer shell
3. The energy difference between the inner and outer shell is balanced by the emission of a photon (X-ray fluorescence radiation)

- The energy, and therefore the wavelength, of the X-ray fluorescence radiation is characteristic for the different chemical elements.

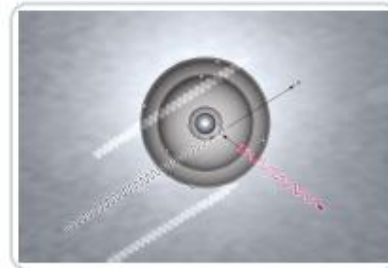
#### QUALITATIVE ANALYSIS

- The intensity of the X-ray fluorescence radiation is, in first approximation, proportional to the element concentration.

#### QUANTITATIVE ANALYSIS



Low Z

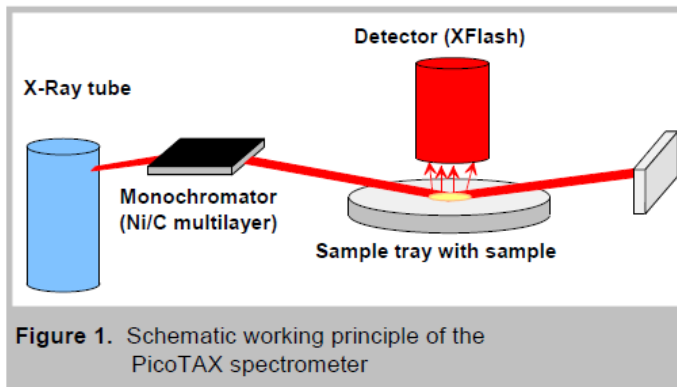


High Z

### TXRF analysis using the PicoTAX:

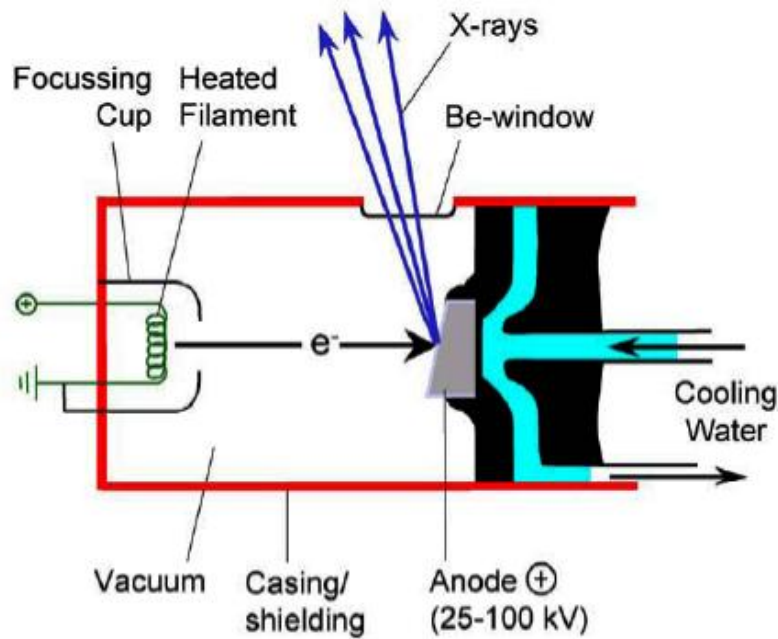
The working principle of Total reflection X-Ray Fluorescence spectroscopy as realized in the PicoTAX spectrometer is shown in **Figure 1**.





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 ( $0.3 - 0.6^\circ$ ) 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.

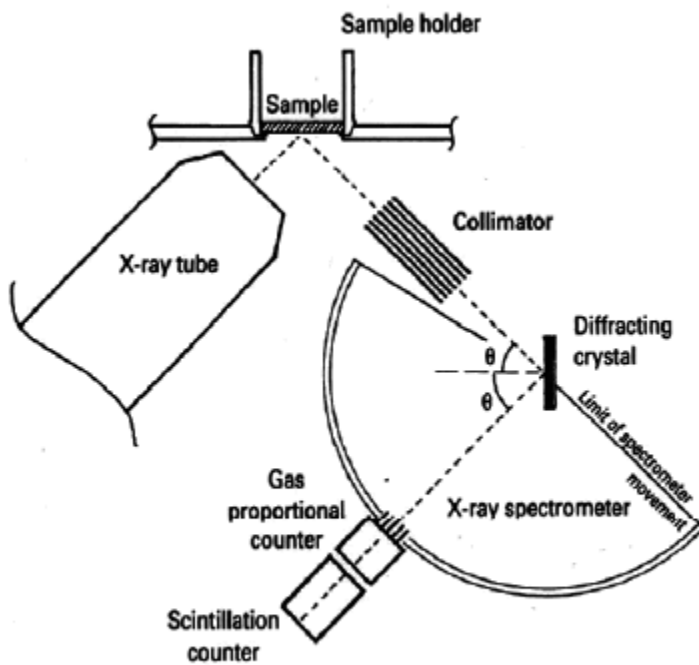


Cross-section of a sealed X-ray tube.

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.



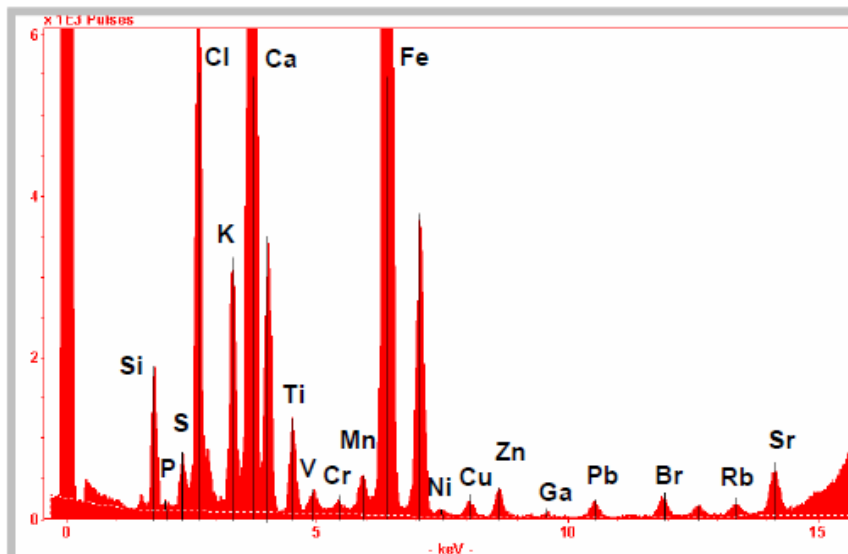


**Schematic drawing of a wavelength-dispersive XRF spectrometer.**

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

**Table 1.** Technical parameters of the PicoTAX spectrometer

|                 |  |
|-----------------|--|
| <b>Tube</b>     | Metal-ceramic (50 W)<br>Air-cooled<br>Mo-Anode                       |
| <b>Optics</b>   | Ni/C-Monochromator (17,5 keV)  |
| <b>Detector</b> | XFlash®<br>Area: 10 mm <sup>2</sup><br>FWHM: < 160 eV @ MnK $\alpha$ |
| <b>Size</b>     | 41,2 x 59,0 x 30,0 cm  |
| <b>Weight</b>   | 37 kg  |



**Figure 2.** Typical energy dispersive spectra of the PicoTAX

## Sample types and preparation:

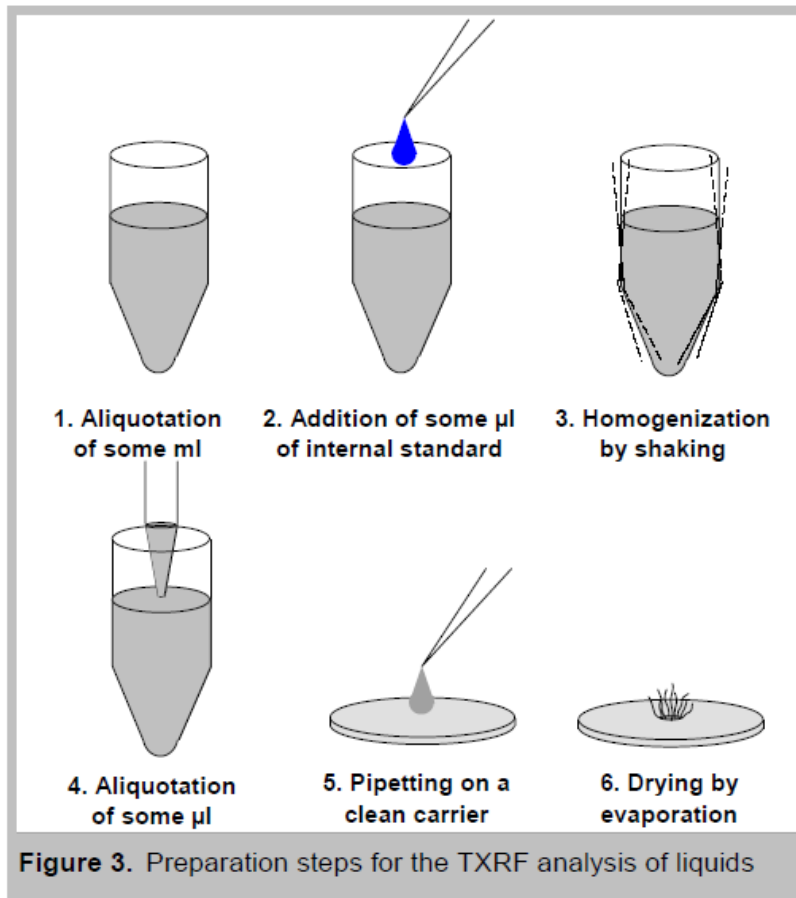
A summary of samples types, which can be analyzed by means of TXRF is given in **Table 1**, showing the great variety of applications.

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 30mm, made of acrylic or quartz glass is common.

**Table 2:** Sample materials analyzable by TXRF  
(KLOCKENKÄMPFER, 1997)

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

Liquids can be perpetrated directly on the sample tray. An amount of several  $\mu\text{l}$  is transferred to the glass disc using a pipette and subsequently evaporated in desiccators 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  $\mu\text{g}$  of sample material are transferred, using a Q-tip or a lint-free tissue.

In a similar way the direct preparation of single micro samples (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:

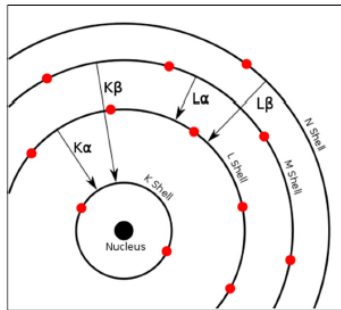
In general all elements starting from Sodium up to Uranium (excl. Niobium, Molybdenum and Technetium) can be analyzed by the PicoTAX (**Figure 4**).

|    |    |  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|--|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| H  |    |  |    |    |    |    |    |    |    |    |    |    |    |    |    |    | He |
| Li | Be |  |    |    |    |    |    |    |    |    |    | B  | C  | N  | O  | F  | Ne |
| Na | Mg |  |    |    |    |    |    |    |    |    |    | Al | Si | P  | Se | Cl | Ar |
| K  | Ca | Sc   | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y  | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I  | Xe |
| Cs | Ba | L  | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | A  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|    | L  | La   | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |    |
|    | A  | Ac   | Th | Pa | U  | Np | Pu | Am | Cm | Ek | Cf | Es | Fm | Md | No | Lr |    |
|    |    | <p>Impossible to measure</p> <p>Difficult to measure</p> <p>Measured using K-lines</p> <p>Measured using L-lines</p> |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |

**Figure 4.** Overview of the measurability of elements using the PicoTAX spectrometer

Each element shows a specific line pattern in a spectrum depending on the orbitals involved

- L→K transition =  $K\alpha$  line
- M→K transition =  $K\beta$  line
- M→L transition =  $L\alpha$  line
- N→L transition =  $L\beta$  line



### Typical TXRF Results Multi-element standard

| Element | Conc./(mg/l) | LLD/(mg/l) |
|---------|--------------|------------|
| Ca      | 0.991        | 0.003      |
| Ti      | 0.997        | 0.003      |
| V       | 0.986        | 0.002      |
| Cr      | 0.994        | 0.002      |
| Mn      | 1.015        | 0.002      |
| Fe      | 0.996        | 0.001      |
| Co      | 1.006        | 0.001      |
| Ni      | 1.005        | 0.001      |
| Cu      | 1            | 0.001      |
| Zn      | 0.989        | 0.001      |
| As      | 1.019        | 0          |
| Se      | 1.1          | 0          |
| Sr      | 0.987        | 0          |

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:

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

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.

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

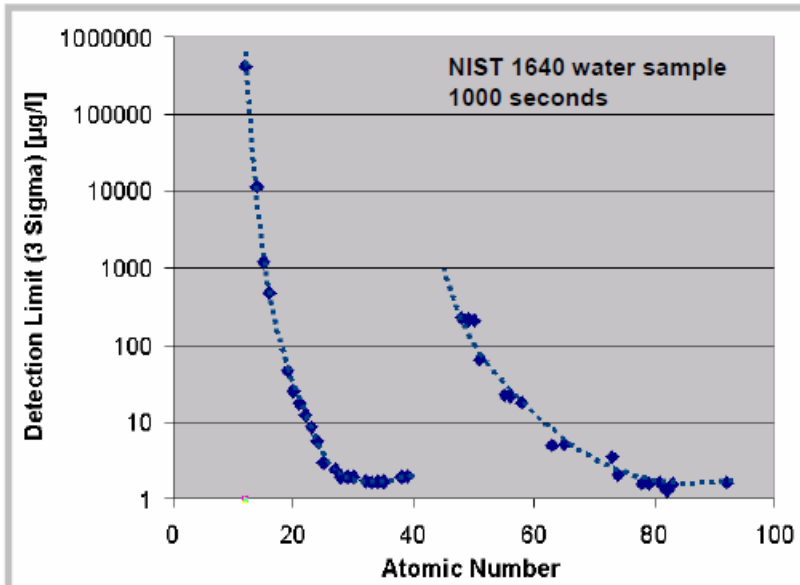


Figure 5. Low Limits of Detection for the PicoTAX

**Table Comparison among TXRF, AAS and ICP characteristics**

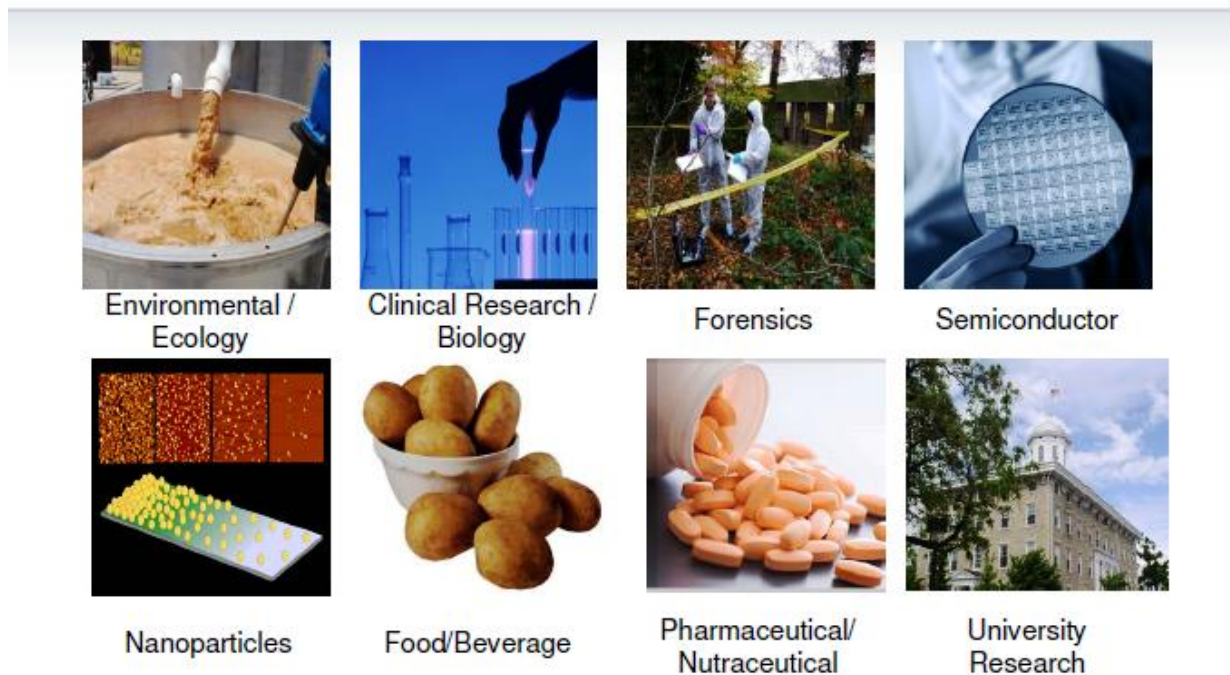
| <b>Property</b>               | <b>TXRF</b>  | <b>AAS</b>  | <b>ICP</b>  |
|-------------------------------|--|---|---|
| <b>Technique used</b>         | <b>Non-destructive technique</b>                     | <b>Destructive technique (digestion required)</b> | <b>Destructive technique (digestion required)</b> |
| <b>Calibration</b>            | <b>Single standard calibration (internal)</b>        | <b>Multi standard calibration (external)</b>      | <b>Multi standard calibration (external)</b>      |
| <b>Sample presentation</b>    | <b>Solutions, suspensions, particles, thin films</b> | <b>Fully dissolved</b>                            | <b>Fully dissolved</b>                            |
| <b>Multi-element analysis</b> | <b>Yes</b>   | <b>Sequential only</b>                            | <b>Yes</b>  |
| <b>Measuring time</b>         | <b>300 – 1000 s</b>                                  | <b>&lt; 10 s for each element</b>                 | <b>&lt; 10 s for each element</b>                 |
| <b>Digestion procedure</b>    | <b>Not necessary</b>                                 | <b>Yes</b>  | <b>Yes</b>  |

## 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.

## Current research areas



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