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Total Reflection X-ray Fluorescence

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List of Definitions and Units

Refractive index n no units

Decrement of dispersion δ no units

Attenuation β no units

Critical angle φ_c [°]

Energy E [keV]

Atomic Mass A [g mol⁻¹]

Atomic number Z no units

Density ρ [g cm⁻³]

Reflectivity R [%]

Penetration depth z_p [10⁻⁹ m]

Wavelength λ [10⁻⁹ m]

Intensity I [counts]

Sensitivity S arbitrary units

Concentration [g L⁻¹]

Introduction

Total reflection X-ray fluorescence spectrometry (TXRF) is a trace elemental micro analysis technique based on conventional energy dispersive X-ray fluorescence. It has become increasingly popular in the last few decades and is applied in almost every field of trace elemental analysis where low detection limits and multi element capabilities are required. Like all X-ray techniques TXRF is non-destructive making it highly useful and important in areas where samples are precious and/or need to be available for further characterization. The ability of probing extremely small sample amounts makes TXRF a superior analytical technique for samples of limited amount. New table top instruments make this technique affordable and versatile as it can be used for field research as well as process monitoring in industrial settings without requirements like vacuum or cooling water circuits. In the semi-conductor industry TXRF is routinely applied to scan wafers for impurities on the surface and in near surface layers.⁹ This article introduces the basic principle of TXRF, its instrumental features, and discusses various applications of this technique. For a more in-depth treatment of the topic the reader is referred to the book of Klockenkämper and von Bohlen and the reviews of Strelt and Wobrauschek listed under suggested further reading.^{16–18}

Basic Principle

Total Reflection, Reflectivity, and Penetration Depth

When an X-ray beam strikes the surface of a solid medium at a certain angle φ it can be refracted or reflected. According to Snell's law the refractive indices n of two media 1 and 2 are in the following relationship:

$$n_1 \cos \varphi_1 = n_2 \cos \varphi_2 \quad (1)$$

In case absorption has to be considered the refractive index n consists of a real part δ and an imaginary part $i\beta$. The real part refers to the decrement of dispersion and the imaginary part to the attenuation:

$$n = 1 - \delta - i\beta \quad (2)$$

[☆] *Change History:* September 2018. Martina Schmeling updated the abstract, introduction, instrumentation, analytical performance, applications and references have been updated and extended, as well as Figs. 3, 5 and Table 3 updated and further reading added. The instrumentation, applications, and further reading parts have been updated as well as Figs. 1, 2, 3, 5, 7 and Table 3. This is an update of Martina Schmeling, Total Reflection X-Ray Fluorescence, Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Elsevier, 2013.

Table 1 Critical angles φ_c , reflectivity R and penetration depth z_p at the critical angle for selected materials calculated for 17.44 keV (Mo $K\alpha$) incident beam energy

Material	φ_c ($^\circ$)	R (%)	z_p (nm)
Plexiglass	0.076	93.2	241
Glassy carbon	0.08	93.9	255
Boron nitride	0.1	93.3	188
Quartz glass	0.1	85.5	83
Aluminum	0.11	82.9	64
Silicon	0.1	81.5	62
Cobalt	0.19	59.1	12.7
Nickel	0.2	58.1	12.1
Copper	0.19	56.1	11.5
Germanium	0.15	51.2	13.1
Gallium arsenide	0.15	51.1	13.0
Platinum	0.28	39.4	4.8
Gold	0.26	38.7	5.0

For X-rays both, δ and β , are zero in vacuum or air, but slightly positive for solids. Thus any solid medium does have a refractive index n smaller than one and is optically less dense than air (vacuum). As a result the refracted beam will be deflected towards the medium boundary and a critical angle will exist at which total reflection of the X-ray beam occurs. Using Snell's law (1) the critical angle φ_c can be calculated for a medium of known composition by using Eq. (3):

$$\varphi_c = \sqrt{(2\delta)} = (1.65E^{-1})\sqrt{ZA^{-1}\rho} \quad (3)$$

With E being the energy in keV, A the atomic mass in g mol^{-1} , Z the atomic number and ρ the density in g cm^{-3} . At the critical angle the reflectivity R of the material increases to almost 100% and the penetration depth z_p of the primary beam decreases drastically to only a few nanometer. Calculation of the reflectivity R can be done for any material by using the Fresnel formula. The penetration depth z_p refers to the depth at which the intensity of the primary beam decreases to e^{-1} or 37% of its initial value. Below the critical angle the reflectivity remains high and the penetration depth low. However, once the critical angle is exceeded both change, with penetration depth increasing and reflectivity decreasing rapidly. The very low penetration depth of the incident beam at and below the critical angle makes total reflection X-ray fluorescence well suited for analysis of matter deposited on and embedded in the uppermost atomic layers of a solid medium.²

In Table 1 critical angles, reflectivity and penetration depth of some common materials used in total reflection X-ray analysis are summarized for an excitation energy of 17.44 keV, corresponding to Mo K excitation. The table shows that the reflectivity for materials composed of light elements is high, but decreases for heavier elements. In the latter case absorption effects become more prominent and affect the reflectivity negatively.

Standing Waves

Total reflection X-ray fluorescence is intimately connected to a standing wave field created by interference of incident and total reflected beam near or at the critical angle. For a thick flat medium, superposition of two or more coherent and monochromatic X-ray beams leads to a triangular standing wave field with minima (nodes) and maxima (antinodes) in front of the medium. Fig. 1 shows such a standing wave field schematically in front of a thick substrate. For a reflectivity of nearly 100% the amplitude of incoming and total reflected wave can be subtracted to zero (nodes) or added to a maximum value (antinodes). Minima and maxima follow each other with a period of $d_{\min/\max} = (\lambda/2) \varphi^{-1}$. Here λ is the wavelength and φ the angle of the incident beam. A layer or sample deposited on top of the thick flat substrate is subjected to this standing wave field and is excited to fluorescence in proportion to the wave field intensity. It is therefore important that the sample is positioned well inside the standing wave field to gain maximum fluorescence of the sample. In addition the sample should be granular or uneven otherwise total

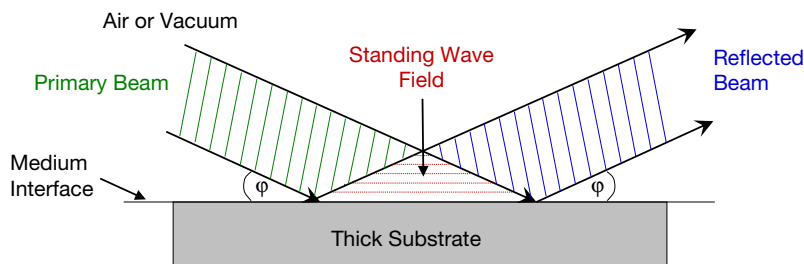


Fig. 1 Standing wave field above a thick flat substrate. φ refers to the grazing angle of the incident and total reflected beam.

reflection inside the deposit might occur. Too large and too thick samples should be avoided as well because absorption effects might interfere.

When a thin enough layer is present on a thick substrate an additional standing wave field can be observed in the thin layer itself beside the one in front of the substrate. When these conditions are fulfilled it is possible to probe surface layers opening up the field for surface and thin layer characterization.

Fluorescence Intensity of Samples Deposited on Top of a Substrate and Below the Surface

A sample deposited on a thick flat substrate is exposed to both, the incident and total reflected beam. Since the reflectivity R is nearly 100% below and at the critical angle, the fluorescence intensity I is almost doubled according to Eq. (4):

$$I = I_0(1 + R) \quad (4)$$

I_0 is the intensity of the incoming X-ray beam at glancing angles. For a granular residue the fluorescence intensity is nearly constant below and at the critical angle. Fig. 2A illustrates that case. The background signal for such sample is extremely low as the incident beam only penetrates a few nanometers into the substrate and does not contribute significantly to the background signal. For example for quartz, silicon or plexiglass® the background signal is about six orders of magnitude smaller than for conventional X-ray fluorescence. This increase in fluorescence intensity is responsible for the high detection power and correspondingly low detection limits of TXRF.²

In Fig. 2B the fluorescence intensity at different glancing angles for atoms embedded in a near surface layer is shown. As seen the fluorescence intensity is clearly angle dependent and experiences a maximum at the critical angle. This feature can be exploited to probe surface layers at different angles around the critical angle and obtain useful information about their composition and thickness. Important is that the layer is non reflective and homogenous in composition. The angle dependency of the fluorescence intensity permits for depth profiling of layered structures as well. The instrumental set-up for these applications is slightly different then for samples deposited on top of the substrate as it requires a mechanism to change the incident angle in small increments. Surface layer characterization is pertinent in the semiconductor industry where contaminations on wafers have to be determined to avoid malfunction of electronic devices.⁹

Instrumentation

The general instrumental set-up for total reflection X-ray fluorescence is quite simple with an X-ray source, a reflector or monochromator, a second reflector, acting as sample support or sample itself and a detector. A low pass filter to reduce the high energy part of the X-ray spectrum maybe inserted into the path of the primary beam to avoid a high background signal due to scattered photons, but is not required for modern devices employing metal ceramic X-ray tubes. Fig. 3 shows such basic instrumental set-up. Conditions for successful excitation of the sample under total reflection are a monochromatic well collimated primary X-ray beam with a divergence of less than 0.2 mrad. The beam is shaped like a strip of paper having a width of about 10 mm and a height of 10 μm to penetrate only a small area of the substrate. The fluorescence radiation is viewed by a small detector, normally 1–3 cm in diameter. The beam can be shaped precisely using slits or diaphragms in the optical path. When analysis of small deposits on a thick substrate is performed the incident angle should be somewhat less than the critical angle of total reflection, that is, about 70% of that angle. In most cases this corresponds to an incidence angle of about 0.06–0.07 degrees or 1.05–1.22 mrad for the primary beam. Flushing the

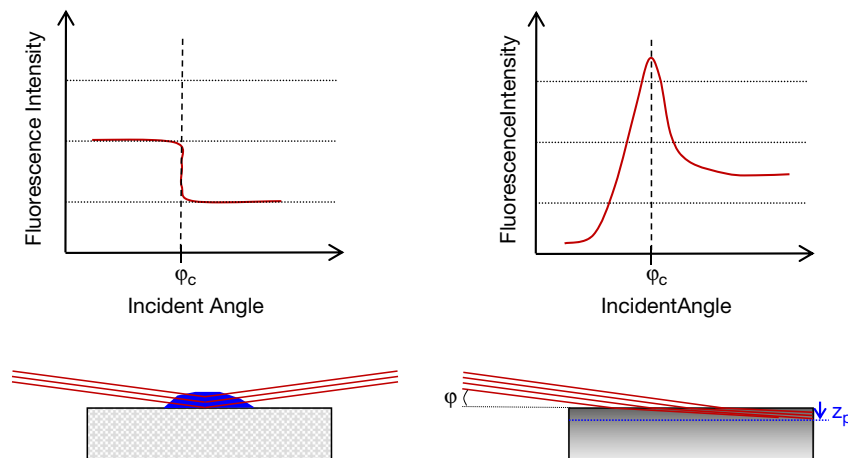


Fig. 2 Fluorescence intensity in dependency of the incident angle φ . For (A) a deposit on a flat thick substrate and (B) atoms present in a surface layer; z_p refers to the penetration depth of the incident beam.

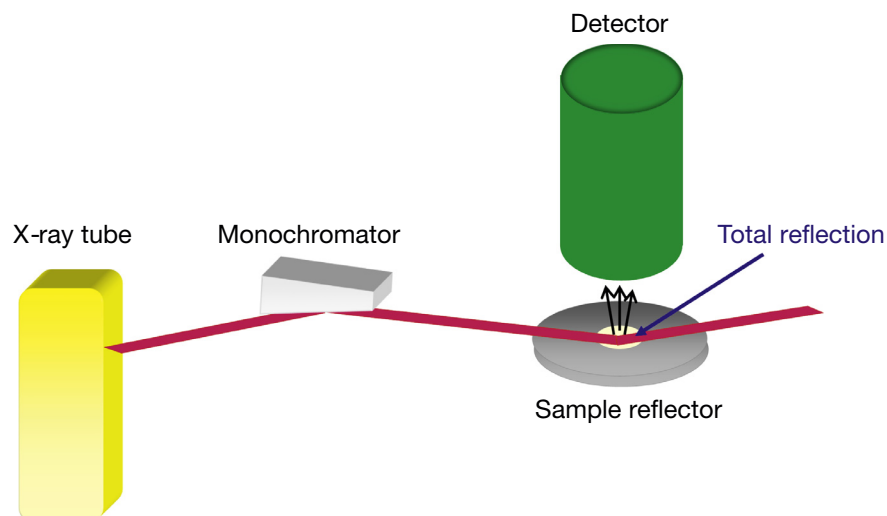


Fig. 3 Basic set-up for a total reflection X-ray fluorescence spectrometer.

sample chamber with nitrogen or helium removes the argon signal from the air present in the chamber and permits for detection of elements such as silver and cadmium. In some special cases when light elements with atomic numbers less than 12 are of interest the optical path, including sample support (or second reflector), has to be under vacuum conditions. This translates to attaching the X-ray source and the detector with a flange to a vacuum chamber in which the sample and optics will be placed. A similar approach is used when working with synchrotron radiation as excitation source.

For surface analysis the instrument should be equipped with a mechanism permitting the variation of the sample position in small increments around the critical angle of the incident beam.

Excitation Devices

A high intensity X-ray beam is necessary to excite the atoms in the sample to fluorescence. For trace and micro analysis of deposits water cooled fine focus or air cooled metal ceramic X-ray tubes are used. Both have sufficiently limiting sizes of the primary beam. Common anode materials are molybdenum, tungsten or chromium, with molybdenum providing most versatility due to its widest energy range for elemental detection without change of tube conditions. Chromium or also scandium anodes are recommended for detection of light elements in combination with a vacuum chamber. When performing surface analysis rotating anodes are recommended to satisfy the demand for lower detection limits. Rotating anodes show higher brilliance and better intensity, thus improving the detection power.⁹ In recent years, synchrotron radiation has become more easily available. Its high brilliance and polarization allows for extremely low detection limits. In addition the energy of the incident beam can be tuned with a multilayer crystal and the width of the beam manipulated with a slit allowing for step wise surface probing. The instrumental set-up resembles closely the vacuum version, except that it has to be tilted by 90 degrees owing to the polarization of the synchrotron beam in the horizontal plane. Several beam lines at different synchrotron facilities are now available for TXRF analysis.

Monochromators

The polychromatic X-ray beam has to be monochromatized to be efficient in excitation of the sample. It is necessary to eliminate the high energy part of the beam which would be scattered in the sample causing an increase in the background signal. In trace and micro analysis highly polished quartz prism or multilayers are employed for this purpose and are inserted into the optical path such that the X-ray beam strikes under grazing incidence and the device acts as total reflecting mirror. In addition a thin metal foil may be inserted into the beam path to attenuate certain energies. For surface and thin layer analysis the X-ray beam has to be strictly monochromatic to obtain good intensity profiles in dependency of the glancing angle. X-ray photons of different energies would interfere with this process and obstruct the angle scan. In this case natural crystals or multilayers are required as monochromatizing units. When natural crystals are used the spectral selectivity is higher but the intensity of the incident beam decreases. To compensate for the loss in intensity rotating anode devices have to be employed. Multilayers on the other hand show less spectral selectivity but permit for a higher intensity. One possibility to increase the selectivity for the latter set-up is the use of two multilayers arranged in parallel position to guide the beam in a zigzag path towards the sample.

Sample Positioning and Detectors

Exceptional care has to be taken with respect to sample positioning in a TXRF unit. Positioning of the sample needs to be extremely precise as the incident angle is very small with less than 0.1 degree. For trace and micro analysis a fixed sample position is realized with a precise positioning mechanism placing the sample exactly at the same spot for each analysis. In surface and thin layer analysis sample positioning is even more crucial as the sample has to be moved with respect to the critical angle. For this the sample is placed on a movable table or stage, which can be rotated, tilted and adjusted in the horizontal x,y direction in small steps to allow for surface screening. The sample support or the sample itself in the case of surface analysis should be optically flat to permit total reflection of the primary beam. The surface roughness has to be restricted to less than 5 nm and the waviness should not exceed 0.001 degree. If using a sample support it has to be free of contamination and chemically inert when performing trace analysis. Materials meeting these requirements and most commonly used are quartz, plexiglass[®] or polycarbonate, glassy carbon, silicone and sapphire. Ultrathin supports such as silicon nitride (Si_3N_4) also satisfy the requirements. Some of these can be cleaned and reused for many analyses without losing their properties.

Detection of the spectra is carried out by a Si(Li) detector or a silicon drift detector (SDD) placed directly on top of the sample at 90 degree angle and at a distance of a few millimeter to obtain a large solid angle. This ensures that the maximum amount of fluorescence radiation is captured by the detector. In addition it minimizes the absorption of soft X-rays in the space between detector and sample. For analysis of light elements a high purity germanium detector with or without beryllium window is recommended having a better spectral resolution in the low energy range.

Analytical Performance

TXRF as a multi element micro analysis technique is capable of analyzing trace or even ultra-trace quantities in samples. A sample has to be small with a mass of no more than a few μg and thin (about 10–15 μm thick) to permit penetration of the primary beam into the substrate for total reflection. Matrix effects are few or nonexistent as a result of the small sample size hence eliminating absorption effects within the sample. Typically some sample preparation is required to obtain a homogeneous analyte and to restrict its mass and size. Sometimes, however, a sample can be analyzed directly. This might be the case for homogenous powders of very fine grain sizes or for thin sections of biological tissues. Owing to its surface sensitivity TXRF can be applied for surface and thin layer analysis. This is of particular interest for determination of impurities or contaminations on wafers. In this case variation of the glancing incident angle provides angle profiles of intensity levels. The detection limits are very low and comparable to most common analytical techniques used in atomic spectroscopy and surface characterization.

Calibration and Quantification

Before quantitative analysis is possible the system has to be calibrated. For this, elemental profiles of each element are measured to obtain their net intensities. This includes preparation of single element standards with concentrations of 1–10 $\mu\text{g L}^{-1}$ in ultra clean water and pipetting a 50–100 μL aliquot of this solution on a sample support or reflector in several steps. The spectrum is recorded and added to the data base. Such calibration needs to be done only once for each instrument as long as the components are not altered or exchanged in the equipment. More recent instruments are equipped with a software package enabling the calculation of the net intensities by using special convolution techniques. This has the advantage that only few element profiles need to be measured.

Graphing of elemental concentration versus measured net intensity N shows a straight line with a slope representing the absolute sensitivity of this element. In Fig. 4 intensities of some elements are shown. The relative sensitivity S_x for an element x is an important parameter and can be determined by the following equation:

$$S_x = (N_x c_x^{-1}) (N_{\text{ref}} c_{\text{ref}}^{-1})^{-1} S_{\text{ref}} \quad (5)$$

With N_x and N_{ref} referring to the net intensity for element x and reference element (ref) and c_x and c_{ref} to the concentration of these, respectively. It is also possible to obtain relative sensitivities mathematically without intensity measurements. Several factors are incorporated in the equation including fluorescence yield and relative emission rate. When elemental standards are not available for certain elements the relative sensitivity can be calculated by applying the above mentioned equations.

Quantification is easy by adding an internal standard of known concentration to the sample either before sample preparation or when analyzing powder samples as a droplet on top of the powder. It was found that the elemental distribution is homogeneous when using an internal standard as long as the sample amount is small and little matrix is present.⁵ The internal standard consists of an element not present in the sample and its concentration should be somewhere in the medium concentration range of all elements to be determined. Most commonly used internal standard elements are gallium and yttrium as both elements typically do not interfere with elements to be determined in the sample. In some cases when the sample is present in basic solution germanium can be added as internal standard. Care has to be taken when elements have to be quantified at ultra trace levels, which are located at energies close to the internal standard. In such situations the internal standard concentration should be as low as possible or a different element should be selected. A "blank run" without standard helps to estimate the concentration level of the internal standard. In cases where sample digestion is required the standard should be added before the digestion step to monitor losses. For powder samples the internal standard should be pipetted onto the sample itself and dried for analysis. Elemental concentrations can be calculated easily by using the following Eq. (6):

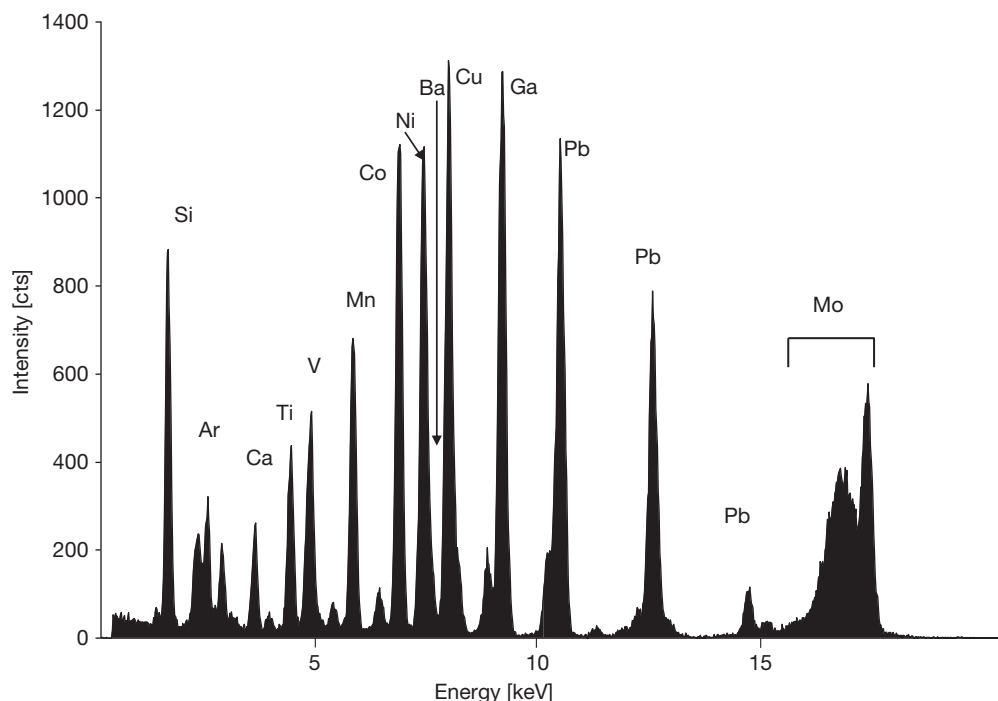


Fig. 4 Intensity profiles for selected elements (Mo K excitation, 20 nanogram concentration). Please note that Ba and Ni overlap slightly.

$$c_x = (N_x S_x^{-1}) (N_{is} S_{is}^{-1})^{-1} c_{is} \quad (6)$$

With c_x and c_{is} referring to the concentrations of the element to be determined and the internal standard (known) respectively, N_x and N_{is} to the net intensities of them as well as S_x and S_{is} to the relative sensitivities.

Calibration and quantification in surface and thin layer analysis has to be performed differently than for micro and trace analysis. It can be done by measuring external standards of pure elements, analyzing dried residues of a standard element or after spin coating of a support or wafer with a spiked solution. Internal standardization is not suitable for quantification as angle variation of the glancing incident beam does influence the fluorescence intensity. An evaluation of the external standardization procedure using nickel as external standard showed that this approach is valid until about 150 ng Ni.⁵ Peak fitting and quantification has to be carried out by using the fundamental parameter method as known for conventional XRF.²

Detection Limits

The detection limits for total reflection X-ray fluorescence are several orders of magnitude lower than for conventional XRF and comparable to most atom-spectrometric methods used for trace analysis or surface characterization such as atomic absorption (AA), inductively coupled plasma optical emission spectrometry (ICP-OES) and laser ablation inductively coupled mass spectrometry (LA-ICPMS). They range from several picogram for most transition metals and heavy elements like lead to a few nanogram for lighter elements in real samples and are somewhat lower for pure aqueous solutions. Improvement of detection limits is possible when the sample is pretreated and/or the matrix removed. This is particularly important when analyzing organic, biological or environmental samples. For surface contaminations the detection limits are around 10^9 atoms $(\text{cm}^2)^{-1}$ for transition metals by direct determination on the surface and can be improved to some 10^7 atoms $(\text{cm}^2)^{-1}$ using special pretreatment techniques like vapor phase deposition. When synchrotron radiation is available as excitation source the detection limits can be pushed further down for direct determination and are reported to be 3×10^8 atoms $(\text{cm}^2)^{-1}$ for Ni directly on a wafer. **Table 2** shows the range of detection limits for commonly analyzed elements.

Table 2 Detection limits for commonly analyzed elements

< 2 pg	2–5 pg	5–10 pg	10–100 pg	> 100 pg
Ni, Cu, Zn, Ga, As, Se	Mn, Fe, Co, Br, Rb, Pb, Bi	Ti, V, Cr, Sr, Y, Zr, Mo, Rb	P, S, Ag, Cd, Sn, Ba, La	Al

Table 3 Scope of applications

<i>Biomedical</i>	<i>Environmental</i>	<i>Industrial</i>	<i>Other</i>
<i>Body fluids</i> Whole blood, serum, urine, amniotic Fluids, enzymes, aqueous humor	<i>Plant materials</i> Lichen, hay, algae, wheat, leaves, moss, needles, wood chips, daphnia	<i>High purity chemicals</i> Acids, water, solvents, salts	<i>Forensics</i> Hair, nails, skin, fibers
<i>Tissue</i> Lung, liver, kidney, colon, breast, brain, human lens	<i>Water</i> Tap water, sea water, waste water, river water, rain, snow <i>Particulate matter</i> Aerosols, fly ash, dust	<i>Metals and ores</i> Aluminum, iron, steel, ores, rocks, powders <i>Oils and greases</i> Crude oil, vegetable oil, essential oil, fat, grease, cream	<i>Art</i> Pigments, oil paints, inks, varnishes <i>Food and Pharmaceuticals</i> Wine, beer, mineral water, fish, mussel tissue, tablets, vegetables, fruits, nuts, food, additives, vaccines
	<i>Other</i> Mud, sediment, sewage, sludge, peat, soil, biofilm, space returned materials, zebrafish	<i>Thin deposits</i> Films, foils, layers, Residues, implants, nanostructures	

Applications

The applications of TXRF are manifold and frequently more are added (⁷). **Table 3** summarizes applications in different fields. Generally, two types of application do exist: micro and trace analysis as well as surface and thin layer analysis. In both cases special care has to be taken that sample preparation and/or analysis is done in very clean environments to avoid possible contamination.

Micro and Trace Analysis

Almost any sample can be analyzed by TXRF for its trace element content either directly or after some sample preparation steps. Such steps might include preconcentration, digestion or matrix separation. Sometimes the samples do not need to be pretreated but can be analyzed directly. Most types of water samples like drinking or tap water, mineral waters, and rain water are sufficiently low in matrix to allow for direct analysis. Atmospheric aerosols or other fine particle samples can be directly deposited on a reflector for trace analysis. Biological and medicinal materials generally need to be pretreated to remove the organic matrix which would increase the background signal and thus worsen the detection limits. Similar steps should be considered for environmental samples containing substantial amounts of matrix like soil or river and sea water. Microwave or high pressure digestion in specially designed Teflon bombs with concentrated high purity nitric acid are the most common pretreatment methods. When silicates are present in a sample a small quantity of hydrofluoric acid can be added to ensure total dissolution. Quantitative analysis of volatile elements like mercury has been achieved by complexation and oxidation.⁴ Mineral oil, vegetable oil or fatty acid containing samples like creams and lotions can be diluted with a solvent or if necessary subjected to cold oxygen plasma ashing to remove excess carbon. In all cases the internal standard should be added before sample preparation steps are performed to avoid errors due to element losses. Tissue samples can be analyzed as thin sections embedded in paraffin or as thin cryogenic sections. With or without pretreatment the sample is deposited on the sample carrier either as a solid or as liquid in small droplet form of about 5–50 μL . Recently, nano and picoliter dispensing systems have been introduced. These units are based on inkjet technologies and deliver single nano or picoliter droplets as well as droplet arrays. The small size of the droplets avoids absorption effects and permits for a homogeneous element distribution (^{11,15}). For a solid sample the analysis can be performed directly whereas the liquid has to be dried either under IR-light or on a hot plate before analysis. Care has to be taken that the dried residue is homogeneous in appearance to avoid pockets of higher and lower concentration. In case of an uneven residue sample pretreatment such as dilution or digestion should be considered to improve the accuracy of data and detection limits. Counting times range between 100 and 1000 s and depend on the concentrations to be determined. The general procedure for trace and ultra-trace analysis has been summarized in **Fig. 5**. **Fig. 6** displays the spectrum of an atmospheric aerosol sample after microwave digestion with nitric acid. Here gallium was added as internal standard.

Surface and Thin-Layer Analysis

Surface analysis is possible when the samples are even and optically flat. Ideally suited for this are wafers as produced and used in the semiconductor industry. Both, uncoated or coated wafers can be characterized. For uncoated wafers surface analysis is performed whereas thin layer analysis is applied for coated wafers. In both cases intensity profiles in dependency of the incident angle around the critical one are recorded. The profiles, also called angle scans, provide information about the elemental composition and thickness of the surface layer. When scanning at different areas of the wafer a surface map of the wafer can be obtained. In practice some

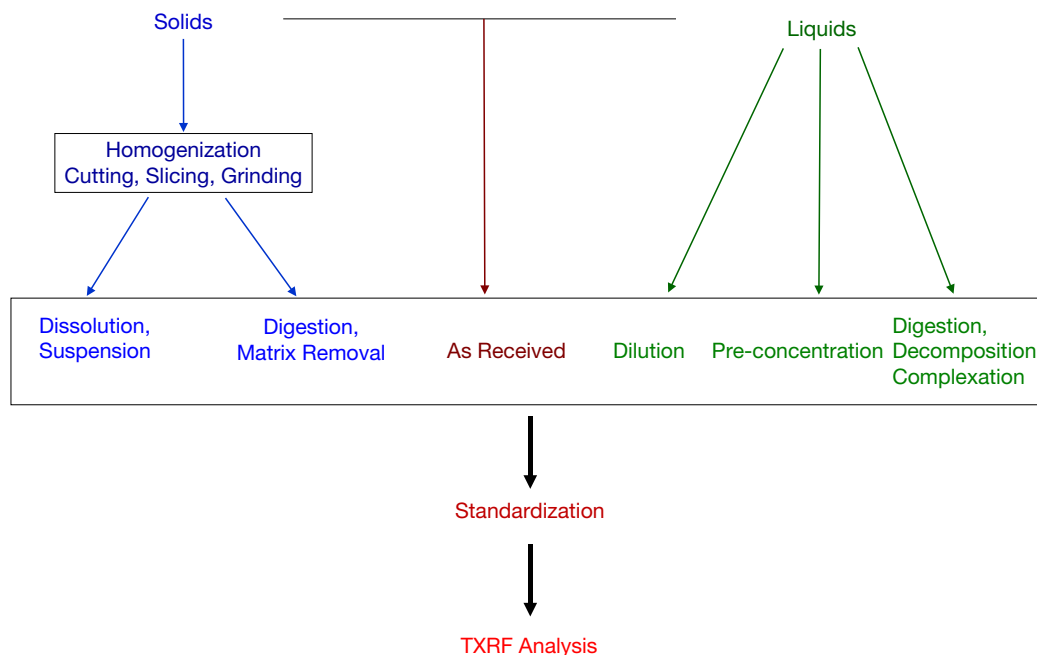


Fig. 5 General sample preparation steps for TXRF analysis.

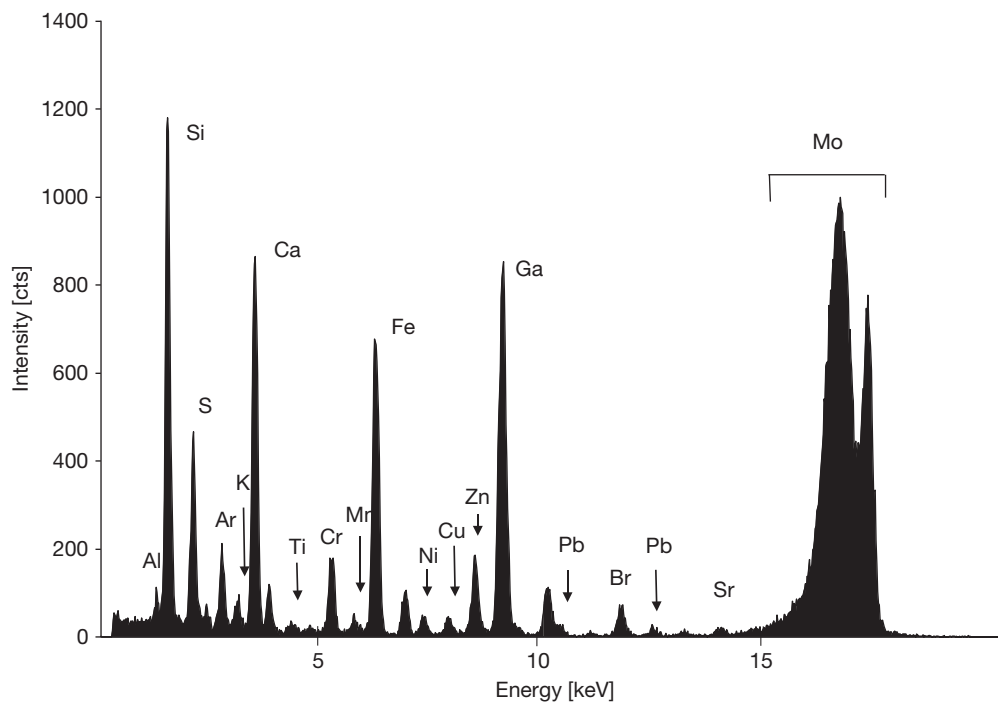


Fig. 6 Spectrum of an urban aerosol sample taken in Chicago. Gallium was added as internal standard with the concentration of $100 \mu\text{g L}^{-1}$.

spots are selected and angle scans performed for those. Angle scans provide information about different types of contamination—bulk, particulate type deposited on the surface or thin layer type—when compared with calibration samples. **Fig. 7** shows the intensity profiles for these three types of contamination schematically. In thin layer analysis layer parameter can be evaluated via iterative peak fitting procedures utilizing the angle scan. The detection limits for wafer analysis can be improved when the wafer is subjected to vapor phase decomposition (VPD) treatment. In this case the surface is slightly etched by hydrofluoric acid and silica (SiO_2) or silicon metal (Si) are removed as silicone hexafluoride (H_2SiF_6). The reaction also produces water droplets in which the surface contaminants are trapped. These droplets are dried and analyzed by TXRF. Special chambers for VPD are usually employed.

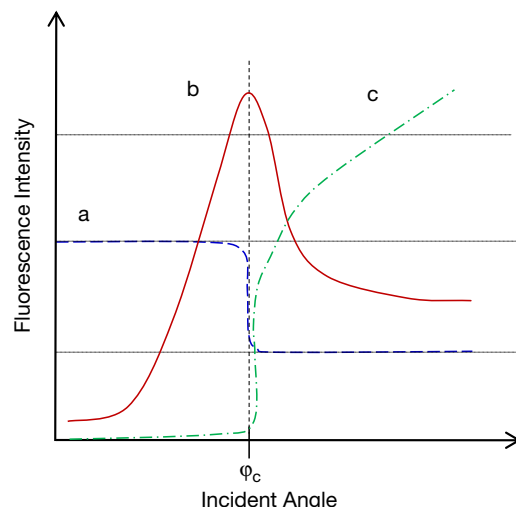


Fig. 7 Intensity profiles for different types of contaminations: (A) particulate type deposit, (B) thin film type deposit and (C) bulk substrate.

Other less common applications of surface analysis include space returned samples and nanostructured materials.^{10,12} In these cases surface scanning was applied to either determine surface contaminants and surface roughness or the orientation of the nanostructures on the surface.

The development and commission of new synchrotron beamlines dedicated to TXRF and GIXRF increased access to these facilities hence enabling applications where ultra-low detection limits, angle scanning capabilities, or tightly focused primary X-ray beams are required. The main applications are in the semiconductor development, but it was also possible to determine abundances of selected solar wind elements in space returned samples using synchrotron radiation as excitation source.^{3,8}

Recent Developments

Besides the more and more popular and accessible use of synchrotron radiation for TXRF two variants of the technique have been emerged in the recent years. One is grazing exit X-ray fluorescence (GEXRF) and the other grazing incidence and exit X-ray fluorescence (GIE-XRF)^(1,13,14). In GEXRF the instrumental set-up has been flipped with having a 90 degrees incident angle, but a grazing take-off or exit angle. In GIE-XRF both angles, the incident and the take-off angle of the beam, are grazing or close to zero. GEXRF can be employed for non-destructive surface and thin-layer analysis in combination with both synchrotron radiation and X-ray tube excitation. It has certain advantages compared to traditional TXRF like permitting a polychromatic incident beam with a lateral resolution of about 10 μm . Surface mapping becomes much faster and easier. In addition a wavelength dispersive detector can be used having a higher spectral resolution and thus showing a better peak separation. The disadvantage is that absorption and matrix effects can occur making quantification difficult. A recently developed compact spectrometer allows for fast trace element analysis in the field or laboratory setting (¹ GIE-XRF is less common and more complicated to set up, but has the advantage that both the incident and the take-off angle can be adjusted. This allows for analysis of thin films and vertical concentration profiles. Other developments include the combination of grazing incidence XRF with X-ray reflectivity (XRR) measurements. GIXRF provides information about elemental distributions within thin layers whereas XRR measures the thickness. The combination of both techniques yielded substantially improved data for ultra-shallow implantations.⁶

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