Materials Characterization by Non-Destructive Methods
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Abstract
The correlation of physical and chemical properties with structural characteristic is important in Materials Science. There are two methods destructive method first and non-destructive second. The destructive method requires dissolution into a fluid phase but non-destructive method does not require it. The non-destructive characterization methods of solid materials can be described in different categories depending upon the type of information required. For elemental analysis, the techniques XRF and EDXRF are used. Structural properties are known by XRD and XPS. To get the information of morphology and topography, SEM and AFM are the recommended techniques.

Qualitative and quantitative characterization techniques for solids are discussed with limitations.

Keywords: Characterizations, EDXRF, XRD and XRF

1. Introduction
Characterization of materials regarding composition, trace impurities, structural phase and crystallographic perfection is vital for repeated reproduction of materials with stringently defined specifications, their applications as well as for fundamental research\(^1\). For characterization of materials a wide variety of techniques and equipment are available. These are based on different principles of Physics and Chemistry and employ modern mathematical analysis and modeling techniques and advanced electronic and information technology facilities.

If the material to be characterized is in gaseous phase, it is sufficient to be concerned with the major and the minor constituents. For liquids it is desirable to get additional information about short range order. The solids can be further sub-divided into single crystals, polycrystalline and amorphous state. Single crystals of interest can have widely different appearances and dimensions. These may be bulk crystals of dimensions going up to 300mm and thin films with thickness going down to nano-metric dimensions\(^2\).

Characterization techniques are different for these types of different situations. Additionally, characterization of a solid surface is required at very high resolution going down to atomic dimensions. Structure of interfaces has become an important area of research as behavior of several devices is strongly influenced by these. A variety of techniques are available for study of crystal defects. These include chemical etching, decoration, field ion microscopy, high resolution electron microscopy, scanning tunneling microscopy and high resolution X-ray diffraction techniques including diffractometry, topography and diffuse
X-ray scattering or reciprocal lattice mapping as it is referred to in recent literature⁴.

2. X-ray fluorescence

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high energy X-rays or gamma rays. This phenomenon is widely used as a fast, accurate and non-destructive method for elemental analysis and chemical analysis.

XRF is today widely used in the fields of metal, cement, oil, polymer, plastic, forensic, mining, mineralogy and geology. For environmental analysis, XRF is able to analyze pollution of heavy metals of water and air. XRF is also widely used in glass, ceramics, research and pharmacy too⁵.

The measurement is fast: typical analysis time is a few seconds per element, and from seconds to half an hour depending on the composition complexity, levels of concentration and requested accuracy. Results are accurate: error can be as low as 0.1% relative if adequate calibration standards are available. When no such standards can be found, semi-quantitative (standardless) analysis remains possible with still good accuracy in many cases. In most cases, XRF analysis is non-destructive, which means that the measured sample can be archived for possible later re-measurement⁵-⁶.

2.1. Basic Working Principle

The basic working principle of an XRF spectrometer is described in Figure 1⁶. An X-ray tube is disposed in front of a sample to be analyzed. XRF fluorescence is a two steps process.

- Step 1: primary photons of sufficient energy are emitted by the X-ray tube and illuminate the sample.
- Step 2: the matter in the sample reacts by emitting fluorescent secondary photons which escape the sample.

The energy (or wavelength or "color") of the fluorescent photons is an indication about the elemental composition of the sample. The intensity of the fluorescent beam (number of photons per sec) is an indication of the element's concentration in the sample.

The goal of the spectrometer is to analyze the fluorescent beam and measure its characteristics in energy (or wavelength) and in intensity. Software coupled to the spectrometer converts this information into concentration's values⁵-⁷.

The way used to analyze the fluorescent beam depends on the spectrometer technology used. There exists fundamentally two different kinds of XRF spectrometers. The EDXRF spectrometer (energy dispersive) discriminates each specific fluorescent line, based on the energy of the fluorescent photon; the WDXRF spectrometer (wavelength dispersive) separates each fluorescent line to a specific reflection angle (a little bit like a prism is used to decompose the various colors of the light spectrum) based on the various wavelengths of the X-ray beam.

X-ray is an electromagnetic radiation: it has a duality of being composed of photons with a given energy and also each photon is associated with a particular wavelength⁷.
Figure 1. Basic principle of XRF spectrometry.

2.2. Advantages of XRF Spectrometer
- All elements of the periodic table from Be to U can be measured qualitatively, semi quantitatively and quantitatively in powders, solids and liquids
- Simple spectra
- Spectral positions are almost independent of the chemical state
- Minimal sample preparation
- It is non-destructive and environmentally friendly analysis method
- Applicable over a wide range of concentrations
- Good precision and accuracy

2.3. Disadvantages of XRF Spectrometer
- X-ray penetration of the sample is limited to the top 0.01 - 0.1 mm layer
- Light elements (below atomic number 22) have very limited sensitivity although C is possible on new instruments
- Inter element (MATRIX) effects may be substantial and require computer correction
- Limits of detection are only modest
- Instrumentation is fairly expensive

2.4. Sample Preparation for XRF Analysis:
Reproducible sample preparation methods are essential. Samples must be in a form that is similar to available standards in terms of matrix, density and particle size.
- Solids, generally solids must be polished as surface roughness may give erratic results.
- Powders and pellets, powdered samples are often pressed into pellets, suspensions may also be analyzed.
- Fusions, with potassium pyrophosphate (K₂P₂O₇) or a tetraborate
(Na$_2$B$_4$O$_7$ or Li$_2$B$_4$O$_7$) present a homogenised sample which can often be analyzed directly.

- Liquids and solutions, an x-ray transparent cover and sample cup must be provided to prevent volatility under vacuum conditions.
- Support media, such as filter paper, millipore filters, ion-exchange membranes.

3. Energy Dispersive EDXRF spectrometer

In an EDXRF (Energy Dispersive) spectrometer, the secondary fluorescent beam emitted by the sample is directly captured by a detector. The detector converts each incoming photon to an electrical impulse. The amplitude of the pulse is directly proportional to the energy of the incoming photon. The impulse goes to an electronic device called MCA (Multi-Channel Analyzer) where it is processed. An MCA should be seen as a computer memory where each memory address is here called a "channel". Each channel is in fact a counter of the numbers of impulse of a specific height submitted to the MCA unit. Prior to a measurement, all channels' memories are cleared.

3.1 Basic Working Principle:

The basic working principle of an XRF spectrometer is described in Figure 2. The working principle of an EDXRF spectrometer is a 3 steps process.

- Step 1: A secondary fluorescence photon is emitted by the sample, under the bombardment of primary photons emitted by the X-ray tube (XRF principle). Secondary photons are emitted in all directions, but we consider here only the directions which bring them to the detector.
- Step 2: The secondary photon enters the detector. It is converted to an electrical impulse. The height (amplitude) of this pulse is directly proportional to the energy of the incoming photon. (In Figure 2, the various energy are represented by different colors: blue means the highest encountered energy, while red is the lowest energy.)
- Step 3: the electrical impulse is processed by the Multi-channel analyzer. This unit determines (measures) the pulse height (via a very fast analog-to-digital converter). The pulse’s height is converted into a specific channel address. The channel memory of concern (in this example, the channel dedicated to the "red energy photons" is then incremented.

Figure 2. EDXRF Spectrometer.
At a given moment, the contents of all channels constitute an image of the measured spectrum. If, we consider that during the measurement (during the period of time where we accumulate counts in the MCA) the measuring condition is fixed (we do not modify the tube kV and mA), one can say that an EDXRF spectrometer is a simultaneous machine. It acquires the information of all elements simultaneously

3.2. Limitation of EDXRF Analysis:

i. Semi-quantification for samples that is not flat, polished, and homogeneous

ii. Size restrictions on samples

iii. Samples must be vacuum compatible (not ideal for organic material)

iv. Analysis (and coating) may spoil subsequent surface analysis

v. Limited sensitivity for low-Z elements

4. X-Ray Diffraction

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.\(^\text{11}\)

4.1. Nature of X-rays

X-rays can be thought of as waves with wavelengths on the order of 0.1 Å to ~10 Å. The shorter wavelength, it is the more energetic wave, because of the relatively short wavelengths of electromagnetic radiation in the X-ray region, X-rays are high energy waves and are much more penetrating compared to UV, visible, IR, or radio waves. The conversion between energy, frequency, and wavelength is the well-known de Broglie relationship: \(E = h\nu = hc/\lambda\), where \(\nu\) is the frequency, \(h\) is Planck’s constant \((6.62 \times 10^{-34} \text{joule-second})\), \(c\) is the speed of light \((2.998 \times 10^8 \text{m/sec})\), and \(\lambda\) is the wavelength of the radiation \((\text{in m})\).

4.2. Generation of X-rays

When electrons strike a metal anode with sufficient energy, X-rays are produced. This process is typically accomplished using a sealed X-ray tube, which consists of a metal target (often copper metal) and a tungsten metal filament, which can be heated by passing a current through it \((\text{typically 10-15 mA})\), resulting in the “boiling off” of electrons from the hot tungsten metal surface. These “hot” electrons are accelerated from the tungsten filament \((\text{negative bias})\) to the metal target \((\text{positive bias})\) by an applied voltage \((\text{typically 15-30 kilovolts})\). The collision between these energetic electrons and electrons in the target atoms results in electron from target atoms being excited out of their core-level orbitals, placing the atom in a short-lived excited state. The atom returns to its ground state by having electrons from lower binding energy levels \((\text{i.e. levels further from the nucleus})\) make transitions to the empty core levels. The difference in energy between these lower and higher binding energy levels is radiated in the form of X-rays. This process results in the production of characteristic X-rays \((\text{i.e. X-rays whose energies are unique to the})\)
target metal due to the quantized nature of the electron energy levels of each atom and the unique energies of these energy levels) \([\text{Cu } K \alpha_1 \text{ (L}_3 \text{ to K electronic transition)}: E = 8047.78 \text{ eV, } \lambda = 1.54051 \text{ Å}, \text{Cu } K \alpha_2 \text{ (L}_2 \text{ to K electronic transition)}: E = 8027.83 \text{ eV, } \lambda = 1.54433 \text{ Å}, \text{Cu } K \beta_1 \text{ (M}_3 \text{ to K electronic transition): } E = 8905.29 \text{ eV, } \lambda = 1.39217 \text{ Å}].\) Thus X-rays provide a convenient means of determining what elements are present in a sample because of the unique wavelengths produced by each unique element. A lower energy process that involves the interaction of electrons with the nucleus of an atom in the target metal produces a continuum of lower intensity X-radiation over a broad energy range known as Bremstrahlung. As the voltage on an X-ray tube is increased, the characteristic line spectra of the target element are superimposed upon the continuous spectrum (Figure 3)\(^1\).

### 4.3. Basic Working Principle

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. X-rays are then detected, processed and counted. By scanning the sample through a range of \(2\theta\) angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the material \(^9\). Schematic of XRD as shown in Figure 4\(^9\).

![Figure 3. X-rays peaks.](image)

![Figure 4. Schematic of XRD.](image)
Table 1. Comparison between XRF, EDXRF and XRD

<table>
<thead>
<tr>
<th>S.#</th>
<th>Technique</th>
<th>Signal Detected</th>
<th>Elements Detected</th>
<th>Detection Limits</th>
<th>Imaging/Mapping</th>
<th>Lateral Resolution/Probe Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>XRF</td>
<td>X-rays</td>
<td>Al-U</td>
<td>10 ppm</td>
<td>No</td>
<td>100 µm</td>
</tr>
<tr>
<td>2</td>
<td>EDXRF</td>
<td>Characteristic x-rays</td>
<td>B-U</td>
<td>0.1 – 1 at%</td>
<td>Yes</td>
<td>&gt;=0.3 µm</td>
</tr>
<tr>
<td>3</td>
<td>XRD</td>
<td>Diffracted x-rays</td>
<td>All elements, assuming they are present in a crystalline matrix</td>
<td>Quantitative multiphase analysis: ~1% External standard quantitative analysis: 0.1% Special quantitative analysis (quartz, polymorphs): ~0.02% Minimum film thickness for phase identification: ~20 Å</td>
<td>No</td>
<td>Point focus: 0.1mm to 0.5mm Line focus 2mm to 12mm</td>
</tr>
</tbody>
</table>

4.4. Experimental Procedure

Sample preparation for X-ray diffraction analysis is an important step of the analysis. Sample must represent the whole material and must be suitable for the sample holder of the equipment. These facts must be taken into account while preparing the samples for the analysis. The sample may be in a bulk or powder form depending on the conditions and desired properties of the sample. If the sample to be analyzed in bulk form then at least one surface of the sample must be perfectly flat. On the other hand, if the sample is in powder form then it must be less than 60 µm in size. If it is coarser than 60 µm, then, it must be milled in a mortar. Then, the sample is placed (if it is in the bulk form) or pressed (if it is in the powder form) into the sample holder. Surface of the sample must be in the same plane with the sample holder and holder must be placed into the XRD equipment very carefully. After placing the sample, the effect of following parameters is going to be studied:

- X-rays tube and sample voltage (for instance 40 kV) and current (for instance 40 mA) values
- receiving slit size,
- scanning speed,
- dwell time at θ values and etc.

4.5. Limitation of XRD Analysis:

- Cannot identify amorphous materials
- No depth profile information
- Minimum spot size of ~50um

5. Comparisons

Any characterization technique has some limitation such as XRF, EDXRF and XRD. Table 1 gives a comparison of
XRF, EDXRF and XRD according to their limitations\textsuperscript{14}.

References


