Energy dispersive X-ray spectroscopy (EDS)
Wavelength dispersive X-ray spectroscopy (WDS)
X-ray spectroscopy

X-ray spectrometers are usually associated with electron microscopes, such as TEM and SEM: these instruments are intrinsically equipped with a cathode and magnetic lenses to create and focus a beam of high-energy electrons onto a specimen. So the installation of an extra X-ray detector results in a spectrometer.

Auger electrons emerge from a very thin region of the sample surface (10 - 50 Å). The volume of characteristic X-ray production is defined by the case where the energy of an electron, $E$, is just sufficient to produce x-rays requiring energy, $E_c$. The critical energy, $E_c$, varies with the X-ray of interest.
Bremstrahlung

Generated when negatively charged electrons in motion are deflected by positively charged atomic nuclei. This involves loss of kinetic energy which is promptly emitted as electromagnetic radiation (X-rays) called white radiation or Bremsstrahlung.

The greater the change in direction the higher the loss of energy and therefore the higher the energy of the outgoing photon.

According to Planck’s equation \( E=\hbar \nu \), the frequency is higher in a higher energy X-ray photon.
Characteristic radiation

Characteristic X-rays are emitted from atomic elements when their electrons make transitions between the inner atomic energy levels.

They occur when a high energy electron ionizes an inner shell (K Shell) electron and then that hole is filled by an outer shell electron.

The other inner layers (L, M, N, …) may also be directly ionized.
X-ray spectroscopy

Nomenclature

K Series:
$K\alpha$ is the line corresponding to an L to K electron transition
$K\beta$ is the line corresponding to an M to K electron transition
$K\gamma$ is the line corresponding to an N to K electron transition

L Series:
$L\alpha$ is the line corresponding to an M to L electron transition
$L\beta$ is the line corresponding to an N to L electron transition
X-ray spectroscopy

Emission spectrum

- Unfiltered in vacuum
- $K_{\alpha}$
- $K_{\beta}$
- Characteristic X-rays
- Bremsstrahlung
- Maximum Photon energy
Each element has characteristic transition energies.
X-ray detector

The central component of an EDS system is a solid-state detector, consisting of a Si(Li) X-ray detector. When a X-ray photon hits the detector, a very small current is produced by knocking out electrons from the semiconductor. Each electron ejected consumes about 3.8 eV of energy from the X-ray. Therefore an X-ray photon starting with 7.471 keV of energy (Ni Kα) will produce a current of about 1966 electrons. By measuring the amount of current produced by each X-ray photon, its energy can be determined.

The detector requires cooling, so that the semiconductor remains suitably doped (high temperature results in species intermixing due to diffusion). During operation (-200 ºC), the dewar must be filled with liquid N₂. Nowadays detectors cooled by Pelletier effect are also available.
Si(Li) semiconductor detectors consist of a 2 to 5 mm thick Si crystal, with gold contacts at its ends. The Si crystal consists of a "Li-drifted" intrinsic region facing the specimen and an adjacent Li-free region. The front contact, Li-drifted intrinsic region, and Li-free region constitute a **p-i-n junction**. A voltage is applied across the detector. The crystal is maintained at low temperatures to prevent diffusion of Li from the intrinsic region to the Li-free region. In general, the diffusion of Li is only a problem when there is a voltage across the detector.

Cross section of a typical lithium-drifted silicon detector. **X-rays create electron-hole pairs in the intrinsic region of the semiconductor**; these charge carriers then migrate to the electrodes under the influence of an applied bias voltage.
Semi-quantitative analysis: (1) Peak identification, (2) background removal, (3) peak deconvolution, (4) ZAF Correction

Z – atomic number
A – Absorption
F – Fluorescence

The interpretation of the EDS spectra is straightforward: the higher the peak the higher the element fraction in the specimen. However, some corrections are needed for a quantitative analysis. As with any spectroscopy: background removal and peak deconvolution are required. Additionally the X-ray generation is strongly dependent on the atomic number and on the type of matrix that surrounds the atom. It is not the same to have a carbon atom embedded in a polymer or in a steel. The X-rays generated by carbon will be much more absorbed if the surrounding matrix is heavy. Furthermore, fluorescence effects also need to be corrected.
EDS — Energy dispersive spectroscopy

ZAF correction

The intensities obtained depend on three matrix effects and must be corrected with theoretical models:

‘Z’ Correction (Atomic Number): The probability of production of an X-ray by an incident electron must account for the probability of backscattering and the average depth of X-ray production, which depend in a complicated manner upon the beam voltage and the average atomic number of the specimen.

‘A’ Correction (Absorption): The probability that an X-ray, once produced, will exit the specimen and reach the detector depends upon the absorption of the overlying material. Each element is characterized by a set of absorption coefficients for X-rays of various energies, and the overall absorption for a specific energy depends thus upon the composition of the specimen as well as the length of the path the exiting X-ray.

‘F’ Correction (Fluorescence): When an emitted characteristic X-ray is absorbed by another matrix element, the absorbing element may be excited and decay with another emission of its own characteristic X-ray. This process, called secondary fluorescence results thus in an intensity enhancement for the fluorescent element and a concomitant intensity decrease corresponding to the primarily excited atom.
EDS – Energy dispersive spectroscopy

Analysis type

• **Qualitative** (element identification, comparison of relative peak heights)

• **Semi-quantitative** (standardless, ZAF correction, higher errors than quantitative)

• **Quantitative** (standards of similar composition)

Spectra interpretation can be done qualitatively by comparison of the peaks, semi-quantitatively if the ZAF correction is used and quantitatively if standard with similar compositions are used.

Semi-quantitative results of a EDS analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.588</td>
<td>1.203</td>
</tr>
<tr>
<td>Si</td>
<td>4.247</td>
<td>2.056</td>
</tr>
<tr>
<td>Ti</td>
<td>0.365</td>
<td>0.301</td>
</tr>
<tr>
<td>Cr</td>
<td>21.793</td>
<td>19.529</td>
</tr>
<tr>
<td>Mn</td>
<td>0.229</td>
<td>0.216</td>
</tr>
<tr>
<td>Fe</td>
<td>3.931</td>
<td>3.783</td>
</tr>
<tr>
<td>Ni</td>
<td>58.337</td>
<td>59.013</td>
</tr>
<tr>
<td>Nb</td>
<td>3.261</td>
<td>5.221</td>
</tr>
<tr>
<td>Mo</td>
<td>5.249</td>
<td>8.677</td>
</tr>
</tbody>
</table>
EDS – Energy dispersive spectroscopy (SEM)

For SEM, the image is built with the signal coming from the X-ray detector, in such a way that only X-rays with a specific energy are used, X-rays maps are produced.
EDS – Advantages and disadvantages

+ The user can quickly collect a full spectrum with the push of a button.

- Low spectral resolution: a Mn Kα X-ray line on an EDS system will typically be between 135-150 eV wide (overlapping of peaks).

- High detection limit, but lower than WDS. Most elements on the periodic table can be measured only into 0.1 weight percent range on the EDS system.
WDS – Wavelength dispersive spectroscopy

• The wavelength dispersive spectrometer is usually coupled with a SEM imaging system and requires dedicated instruments designated by electron microprobe micro-analyzer (EPMA).

• The spectrometer uses **diffraction** to sort by wavelength the characteristic X-rays emitted by the sample. The X-rays are selected using analytical crystals with specific lattice spacing positioned at specific $\theta$ angles. Only the wavelengths that satisfy Bragg’s law are allowed to pass on to the detector.

• The analytical crystals are bent in order to focus the X-ray beam on the sample and on the detector and are situated in the Rowland circle to maximize the collection efficiency of the spectrometer.
WDS vs EDS

- Each element produces a unique set of characteristic X-rays when bombarded with electrons. Each X-ray will have a specific energy and wavelength. Wavelength dispersive spectrometers (WDS) sort the X-rays based on their $\lambda$.

- WDS systems use X-ray diffraction as the means by which they separate X-rays. The spectrometer consists of an analyzing crystal and a detector. Those X-rays that hit the crystal and diffract will enter the detector. An X-ray photon will diffract, depending on its wavelength, the orientation of the crystal and the crystal's lattice spacing. Only X-rays of a given wavelength will enter the detector at a given time. To measure X-rays of another wavelength, the crystal and detector are moved to a new position (new $\theta$). Since a specific WD spectrometer can measure only one X-ray wavelength at a time, it is important that a WDS system has an array of spectrometers in order to work efficiently. Electron microprobes typically have up to five WD spectrometers, allowing them to measure five elements simultaneously. Each spectrometer typically has between two and four analyzing crystals, each with a different lattice spacing, because each type of crystal can diffract only a given range of wavelengths.
WDS – Wavelength dispersive spectroscopy

• Crystals with different $d$ must be used to cover the whole wavelength range.

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>$d$ (Å)</th>
<th>Wavelength range (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium fluoride</td>
<td>LIF</td>
<td>2.013</td>
<td>0.8-3.2</td>
</tr>
<tr>
<td>Pentaerythritol</td>
<td>PET</td>
<td>4.371</td>
<td>1.8-7.0</td>
</tr>
<tr>
<td>Thallium acid phthallate</td>
<td>TAP</td>
<td>12.95</td>
<td>5.1-21.0</td>
</tr>
</tbody>
</table>

• The X-rays are detected in a “proportional counter” consisting of a gas-filled tube with a coaxial anode wire: X-rays ionize gas atoms producing free electrons, which move to the anode while the positive ions move out the cathode; each detected photon produces a charge pulse proportional to the photon energy; the pulses are counted and plotted against the X-ray wavelength.

• WDS requires standard reference materials in concentrations similar to the materials to investigate and is typically used for quantitative spot analysis. The composition of unknown samples is determined by comparing the intensities obtained from the studied samples with those from the standard reference materials. This more complicated technique is complementary to EDS, although wavelength dispersive spectrometers have significantly higher spectral resolution and enhanced quantitative potential.
WDS vs EDS

• One of the main advantages of the EDS system is that the user can quickly collect a full spectrum with the push of a button. Using a WDS system the user must use multiple spectrometers to get the entire periodic table, and has to mechanically scan the spectrometers from one limit to the other.

• WDS has higher spectral resolution. A Mn Kα line on an EDS system will typically be between 135-150 eV wide. On a WDS system, the same X-ray line will only be about 10 eV wide. This means that the overlap between peaks of similar energies is much smaller in the WDS system.

Comparison of spectra collected from a Pt-Au-Nb alloy on EDS and WDS systems. In WDS, six X-ray lines can be identified, with an overlap occurring only for the Au Mα and the Pt Mβ lines. In EDS, the broad nature of the X-ray lines masks everything.

• WDS has lower detection limit. Most elements can be measured into the 0.01 weight percent range on a WDS system and into 0.1 weight percent range on the EDS system. Also, much better performance can be obtained for light element analyses (Be, B, C, N, O and F) on a WDS system. The count rates will be much better, peak overlap problems will be fewer, and reproducibility will be much improved compared to EDS.
EDS and WDS

SEM sample preparation

Coating with conductive film (Au or Carbon)

Heavy metal characteristic peaks tend to interfere with sample characteristic peaks. Carbon coating solves this problem, but the Secondary Electron images are much less contrastful...
Transmission electron microscopy

• TEM is an analytical tool that allows detailed investigation of the morphology, structure and local chemistry of metals, ceramics, polymers, biological materials and minerals.

• It also enables the investigation of crystal structures and crystallographic orientations through electron diffraction, as well as second phase, precipitates and contaminants distribution by X-ray and electron-energy analysis.

• Magnifications of up to 500,000x and detail resolution below 0.2 nm are achieved routinely. Quantitative and qualitative elemental analysis can be provided from features smaller than 10 nm. For crystals with interplanar spacing greater than 0.2 nm, crystal structure, symmetry and orientation can be determined.
The TEM consists of the following major parts:

1. The illumination system
   - Electron gun
   - Condensers

2. The image forming system
   - Objective lens

3. The projective system
   - Several projector lens

4. Apertures
   - Affect the formation of images and diffraction patterns
SEM and TEM
Besides resolution, one of the main advantages of TEM is the ability to perform **diffraction studies** at specific regions as small as tens of nanometers, allowing to determine the crystalline structure of the region.

A diffraction pattern is always formed at the back focal plane of the objective (even in OM). To view this diffraction pattern one has to change the excitation of the intermediate lens. A higher strength projects the specimen image on the screen, a lower strength project the DP.

The optical system of the TEM: The objective lens simultaneously generates the diffraction pattern and the first intermediate image. Note that the ray paths are identical until the intermediate lens, where the field strengths are changed, depending on the desired operation mode. The field strengths can be changed by setting the focal lengths (the distance from the lens to the ray crossover). A **higher field strength** (shorter focal length) is used for **imaging**, whereas a **weaker field strength** (longer focal length) is used for **diffraction**.
TEM imaging vs diffraction

Abbe’s principle of imaging

Rays with same $\theta$ converge

(inverted)
TEM imaging techniques – Contrast mechanisms

The image contrast originates from:

- Diffraction: Crystalline materials
- Phase: High-resolution TEM (atomic resolution)
- Mass (amplitude) contrast: Polymers and biological materials
TEM imaging – Diffraction contrast

**Bright field (metals and ceramics)**

Bright-field imaging is used for examination of most microstructural imaging. In order to examine samples in bright-field, the objective aperture must be inserted. The objective aperture is a metal plate with holes of various sizes machined into it. The aperture is inserted into the back focal plane, the same plane at which the diffraction pattern is formed. The back focal plane is located just below the sample and objective lens. When the aperture is inserted, it only allows the electrons in the transmitted beam to pass and contribute to the resulting bright-field image.

An aperture allows unscattered electrons to proceed and form the image while the scattered ones are blocked. Dark regions are strongly diffracting or dispersing the light. This is the most common imaging technique.
TEM imaging – Diffraction contrast

Bright field (metals and ceramics)

In the bright field (BF) mode of the TEM, an aperture is placed in the back focal plane of the objective lens which allows only the direct beam to pass. In this case, the image results from a weakening of the direct beam by its interaction with the sample.

If the sample has crystalline areas, many electrons are strongly scattered by Bragg diffraction (especially if the crystal is oriented along a zone axis with low indices), and this area appears with dark contrast in the BF image. The scattered electron beams are deflected away from the optical axis and blocked by the objective aperture, and thus the corresponding areas appear dark in the BF-image.
TEM imaging – Diffraction contrast

In dark field (DF) images, the direct beam is blocked by the aperture while one or more diffracted beams are allowed to pass the objective aperture. Since diffracted beams have strongly interacted with the specimen, very useful information is present in DF images, e.g., about planar defects, stacking faults or particle size.
TEM imaging – Diffraction contrast

Dark field (metals and ceramics)

Dark-field images occur when the objective aperture is positioned off-axis from the transmitted beam in order to allow only a diffracted beam to pass. In order to minimize the effects of lens aberration, the diffracted beam is deflected along the optic axis.

One diffracted beam is used to form the image. This is done with the same aperture which is displaced. However, as these electrons are not on the optical axis of the instrument, they will suffer from severe aberrations that will lower the resolution. If an inclined beam is used, the diffracted beam will be at the optical axis.
TEM imaging – Diffraction contrast

**Bright field images**

When an electron beam strikes a sample, some of the electrons pass directly through while others may undergo slight inelastic scattering from the transmitted beam. **Contrast in an image is created by differences in scattering.** By inserting an aperture in the back focal plane, an image can be produced with these transmitted electrons. The resulting image is known as a bright field image. **Bright field images are commonly used to examine micro-structural related features.**

BF image of a twinned crystal in strong contrast. Crystalline defects shown in a BF image.
TEM imaging – Diffraction contrast

Dark field images

If a sample is crystalline, many of the electrons will undergo elastic scattering from the various (hkl) planes. This scattering produces many diffracted beams. If any of these diffracted beams is allowed to pass through the objective aperture a dark field image is obtained. In order to reduce spherical aberration and astigmatism and to improve overall image resolution, the diffracted beam will be deflected such that it lies parallel the optic axis of the microscope. This type of image is said to be a centered dark field image or on-axis dark field image. Dark field images are particularly useful in examining micro-structural detail in single crystalline phases.

DF image of a twinned crystal in strong contrast. Crystalline defects shown in a DF image.
TEM imaging – Phase contrast

Crystalline materials (metals and ceramics)

Here many beams are allowed to pass through the objective aperture (as opposed to bright and dark field where only one beam passes at the time).

To obtain lattice images, a large objective aperture has to be selected that allows many beams including the direct beam to pass. The image is formed by the interference of the diffracted beams with the direct beam (phase contrast). If the point resolution of the microscope is sufficiently high and a suitable crystalline sample oriented along a zone axis, then high-resolution TEM (HRTEM) images are obtained. In many cases, the atomic structure of a specimen can directly be investigated by HRTEM.
An atomic resolution image is formed by the "phase contrast" technique, which exploits the differences in phase among the various electron beams scattered by the sample in order to produce contrast. A large objective lens aperture allows the transmitted beam and at least four diffracted beams to form an image.
TEM imaging – Mass contrast
Bright field (polymers and biological materials)

• Heavy atoms scatter more intensely and at higher angles than light ones.

• Strongly scattered electrons are prevented from forming part of the final image by the objective aperture.

• Regions in the specimen rich in heavy atoms are dark in the image.

• The smaller the aperture size, the higher the contrast.

• Fewer electrons are scattered at high electron accelerating voltages, since they have less time to interact with atomic nuclei in the specimen: High voltages TEM result in lower contrast and also damage polymeric and biological samples.
TEM imaging – Mass contrast

Bright field images
(J.S.J. Vastenhout, Microsc Microanal 8 Suppl. 2, 2002)

In the case of polymer and biological samples, due low atomic number and similar electron densities, staining helps to increase the imaging contrast and improves the radiation damage.

The staining agents work by selective absorption in one of the phases and tends to stain unsaturated C-C bonds (double or triple carbon-carbon bonds). Since they contain heavy elements with a high scattering power, the stained regions appear dark in bright field.

Stained with OsO₄ and RuO₄ vapors
Os and Ru are heavy metals...
TEM techniques: Cryo TEM (requires cooled stage)

- Cryo-TEM permits macromolecules and molecular assemblies to be examined in a native state as much as possible.

- Specimens are suspended in a thin film of water and cooled by immersion in liquid ethane (-140°C) so rapidly that the surrounding water does not have time to crystallize into ice and forms a glass.

- Contrast is low but image processing routines, such as image averaging is used to enhance the signal-to-noise ratio.
TEM techniques: Cryo TEM (requires cooled stage)

Structure of hepatitis B virus solved by cryo-EM
(A) Two-dimensional transmission electron micrographs (projection images) are recorded at different tilt angles for individual 3D objects. The specimen holder is tilted incrementally around an axis perpendicular to the electron beam, and projection images of the same specimen area (field of view) are recorded on a CCD camera at each position. Tilt increments are typically 0.5° to 5° and the tilt range is about ±70°.

(B) Images projected by a specimen at successive tilt angles.

(C) After translationally and rotationally aligning all of these projection images, the imaged object is reconstructed into a 3D density map (often called the tomogram) by a weighted-backprojection procedure.

Analogous to confocal tomography but at much higher resolution and the beam does not scan the sample, instead the sample is tilted.
TEM – Other imaging techniques

Cryo-electron tomography

The 3D ultrastructure of a human erythrocyte infected with *P. Falciparum* (malaria)

(a) Image of a 20-nm-thick slice across a bright-field STEM tomogram obtained from a 1 m-thick section. N, nucleus; FV, food vacuole; LB, lipid body; and CC, circular cleft. (b,c) Rendered 3D model of an infected erythrocyte.

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TEM – Diffraction techniques

Spot Patterns (Selected area diffraction – SAD)

are created when electrons are diffracted in a single crystal region of a given specimen. The center spot corresponds to the transmitted electron beam. Other spots are diffracted portions of the initial electron beam. Spot Patterns can be used for unknown phase identification and identification of crystal structure and orientation. The location of the spots are again governed by Bragg's law.

SAD is a technique to reduce both the area and intensity of the beam contributing to a diffraction pattern by the insertion of an aperture into the image plane of the objective lens. This produces a virtual diaphragm in the plane of the specimen.

Diffraction pattern from a single crystal of silicon in the <111> orientation.
TEM – Diffraction techniques

Indexing spot patterns (Selected area diffraction – SAD)

Figure 3.4. The reciprocal lattice.
Ring Patterns

created when electron diffraction occurs simultaneously from many grains with different orientations relative to the incident electron beam. Analogous to x-ray powder diffraction, ring patterns, can be used to identify unknown phases or characterize the crystallography of a material. The radii and spacing of the rings are governed by:

$$R_d = \lambda L$$

where $d$ is the interplanar spacing, $R$ is the ring radius, and $L$ is known as the camera constant.

Ring diffraction patterns from polycrystalline gold indexed to show which atomic planes (hkl) are contributing to the ring.
Transmission electron microscopy

Ring Diffraction patterns

Crystalline with planar defects

Partially amorphous
Transmission electron microscopy

Structure identification

Simulations
TEM – Sample requisites

Specimens must meet the following requirements:

- Thin enough for electrons to penetrate without excessive energy loss.
- Be representative of the structure and composition.

For penetration of a 200 kV electron beam, a typical metal, ceramic, or semiconductor specimen must be less than 100 nm thick. However, the specimen is required to represent the unaltered bulk material in terms of structure, chemistry, and content of defects. If one also wishes this specimen to have large amounts of electron-transparent thin area, be flat and unbent, and be strong enough to be easily handled, the task of making such a specimen from an arbitrary material is very difficult. Some specimens such as thin films may be examined directly with very little specimen preparation.

In the case of biological samples, the preservation of the fine structures without induced artifacts and the contrast generation are important issues.
TEM – sample preparation

Picking up thin section and deposit onto grid/sample holder

TEM grids (notice the size)

Gatan TEM sample holders
TEM – Sample preparation scheme for metals and ceramics

Mechanical + Ion-Thinning Sample Preparation

Takes between 1 and 30 h and involving the following steps:

- The bulk material is reduced to a disc of 3 mm diameter by sanding, cutting, electro-erosion, crushing or repeated cleaving.

- The preparation of a transparent area on the edge of a specimen by polishing it at a slight (less than 5°) angle is called wedge polishing and is a very common method.

- Dimpling is another common preparation technique. The sample is pre-thinned to 30-50 µm and a bowl-shaped dimple is polished in the center.

- One way of achieving the electron-transparent thickness of 5 µm is ion-milling at a low angle (10° to 15°) to create a transparent area with a centered hole in the specimen.
Advantages vs Disadvantages of TEM

Advantages

- Highest spatial resolution (atomic scale resolution (sub Å))
- Local crystallographic and chemical analysis at very high resolution
- Quantitative identification of structural defects (e.g. determination of dislocation Burgers vector)

Disadvantages

- TEM is an expensive instrument
- Destructive technique (during sample preparation)
- Sample preparation is time consuming
- Some materials are sensitive to electron beam radiation, resulting in a loss of crystallinity and mass
- Sample dimension is small: 3 mm diameter, less than ~100 nm thick for transparency (poor statistical sampling)