Contrasted strengths and weakness of EDS, WDS and AES for determining the composition of samples

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Course 590B

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Iowa State University
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History of EDS and WDS

• By the 1920s, the characteristic X-ray patterns had been recorded for most of the elements

• 1942 - first use of SEM to examine surfaces of thick specimens at RCA Labs at Princeton

• 1949 – Raimond Castaing constructed first electron microprobe for microchemical analysis (Onera) with crystal focusing WDS at École normale supérieure, Paris

  *Application des sondes électroniques à une méthode d'analyse ponctuelle chimique et cristallographique – PhD thesis*

• 1956 - commercial production of electron microprobe began (Cameca)

• 1965 - commercial production of SEM began

• 1968 – solid state EDS detectors developed and first qualitative publication on it was written by Ray Fitzgerald, Klaus Keil and Kurt F.J. Heinrich at University of California, San Diego

  *Solid-state energy-dispersion spectrometer for electron-microprobe x-ray analysis – Science 159, 528 (1968)*

photo of Castaing working on Onera prototype in 1951, anciensonera.fr
photo of Keil with the original Si(Li) detector of EDS, while a modern EDS is shown in background on 40th anniversary of EDS, Microsc. Microanal. 15, 476–483, 2009
History of Auger effect

• 1922 – Lise Meitner discovered the effect as a side effect in her research on radioactivity and nuclear physics at Kaiser Wilhelm Institute, Berlin

  She was the second woman to obtain a doctoral degree in physics at the University of Vienna in 1905. She went to the Friedrich-Wilhelms-Universität in Berlin where famous physicist Max Planck allowed her to attend his lectures, an unusual gesture by Planck, who until then had rejected any woman wanting to attend his lectures. During the first years she worked together with chemist Otto Hahn and together with him discovered several new isotopes.
  In the first part of World War I, she served as a nurse handling X-ray equipment. She was praised by Albert Einstein as the “German Marie Curie”.

• 1923 – Pierre Auger discovered the effect independently at the École normale supérieure in Paris, the year when he passed the agrégation of physics

• 1953 – J. J. Lander made first Auger effect spectrometer in Bell Labs


photo of Lise Meitner, Pierre Auger and Auger electron spectroscopy taken in 1974 at Hanford, wikimedia.org
Origin of X-rays and Auger electrons

Production of X-rays and Auger electrons

- Incident electron knocks inner electron
- Photon is internally converted and another bound electron is ejected from atom
- Upper electron drops to fill the vacancy emitting a photon

X-ray photon

Auger electron

Relative probability of emission

--- X-ray photon emission
— Auger electron emission

illustration: http://hyperphysics.phy-astr.gsu.edu
graph: Handbook of x-ray and ultraviolet photoelectron spectroscopy, D. Briggs, 1977
An ideal x-ray detector would be small, inexpensive, and easy to operate, collect most of the x rays emitted from a sample, have a resolution of the natural x-ray line width being measured (a few electron volts), and be capable of collecting spectral data rapidly without losing information.

Illustration: Nuclear Family of the 1950's, fiftiesweb.com
Quote: Scanning Electron Microscopy and X-Ray Microanalysis, Goldstein, 1992
How do they work?

**EDS**
- solid state detector consisting of semiconductor – Si(Li)

**WDS**
- using crystal diffraction

**AES**
- surface analysis technique
  - sampling depth on the order of 1 nm

- geometry

Bragg’s law \[ n\lambda = 2d \sin \theta \]
Moseley law \[ \lambda \propto \frac{1}{Z^2} \]

*book: Scanning Electron Microscopy and X-Ray Microanalysis, J. Goldstein, 2\textsuperscript{nd} edition*
## When to use which detector?

<table>
<thead>
<tr>
<th>EDS</th>
<th>WDS</th>
<th>AES</th>
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</thead>
<tbody>
<tr>
<td>• Range of elements able to be detected</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Z ≥ 10 – Be window</td>
<td></td>
<td></td>
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<tr>
<td>Z ≥ 4 – thin window or windowless</td>
<td></td>
<td></td>
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<tr>
<td>• for (2.5-15 keV) efficiency ≈ 100%</td>
<td></td>
<td></td>
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<tr>
<td>• for crystal spectrometers efficiency is usually &lt; 30%</td>
<td></td>
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<tr>
<td>• useful range: (0.28-20 keV)</td>
<td></td>
<td></td>
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<tr>
<td>• useful range: (0.1-15 keV)</td>
<td></td>
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<tr>
<td>• Z ≥ 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Z &lt; 10</td>
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- **EDS**
  - Range of elements able to be detected:
    - Z ≥ 10 – Be window
    - Z ≥ 4 – thin window or windowless
  - Energy range of detected X-rays/electrons and efficiency of detection:
    - Depending on inherent detector system and geometric efficiency
  - For (2.5-15 keV) efficiency ≈ 100%
  - At higher energies, a certain percentage of x-ray photons are transmitted through the silicon crystal, while at low energies a certain percentage of photons are absorbed in the window or are also absorbed in the surface dead layer or gold contact layer on the detector crystal
  - Useful range:
    - (0.28-20 keV)

- **WDS**
  - Range of elements able to be detected:
    - Z ≥ 10
  - Energy range of detected X-rays/electrons and efficiency of detection:
    - For crystal spectrometers efficiency is usually < 30%
  - Why? Transmission losses in the proportional counter and partially due to losses in the diffraction crystal
  - Useful range:
    - (0.1-15 keV)

- **AES**
  - Range of elements able to be detected:
    - Z < 10
  - Energy range of detected X-rays/electrons and efficiency of detection:
    - < < 30% maximum efficiency of KLL Auger electron with kinetic energy of 1 keV efficiency is 30%
  - Sensitivity < 1% for one monolayer
  - Useful range:
    - (0.05-3 keV)
  - For which X-ray analysis is least sensitive

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## Measurements

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<tr>
<td><strong>Percentage of energy range covered in 1 measurement</strong></td>
<td>• entire range</td>
<td>• ≈ spectrometer resolution</td>
<td>• entire range</td>
</tr>
<tr>
<td><strong>Maximum count rate</strong></td>
<td>• at optimum resolution is about 2000 to 3000 c/s over the entire energy range</td>
<td>• when tuned to a specific element, count rates up to 50,000 c/s without loss of resolution</td>
<td>• not applicable with SAM</td>
</tr>
<tr>
<td><strong>Data-collection + interpretation time</strong></td>
<td>• minutes</td>
<td>• tens of minutes</td>
<td>• lateral spatial resolution as small as 8 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unless the WDS is specifically programmed to go to peak positions, anywhere from only 1/100 to 1/1000 of the total data-collection time may be associated with the measurement of each individual peak.</td>
<td>• tens of seconds in SAM</td>
</tr>
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Resolution and interpretation

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<td>• about 30 times lower spatial resolution than for WDS (in FWHM)</td>
<td>• high spatial resolution superior peak resolution of elements and sensitivity of trace elements</td>
<td>• Auger peaks appear as small features on intense inelastic background P/B very small</td>
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<td>• P/B ratio for given energy</td>
<td>• better P/B ratio and better spectral dispersion due to crystal spectrometer</td>
<td>• Chemical shifts WHY? e-e interactions, screening, polarization</td>
</tr>
<tr>
<td>WHY? because we need to integrate over some range around peak</td>
<td>• crystal dependent (5 eV)</td>
<td>plots: Oxford Instruments, nano.oxinst.com book: Scanning Electron Microscopy and X-Ray Microanalysis, J. Goldstein, 2nd edition</td>
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**Table:**

- EDS:
  - About 30 times lower spatial resolution than for WDS in FWHM.
  - P/B ratio for given energy.
  - Energy dependent.
  - $FWHM \propto \sqrt{C^2E + N^2}$
    - $C$ – uncertainty of number of formed charge carriers.
    - $N$ – FWHM of electronic noise of the amplification process.
  - $FWHM = \sqrt{2.5(E - E_{ref}) + FWHM_{ref}^2}$
  - $Mn K\alpha$ as measured with a $^{55}Fe$ source (140 eV at 5.9 keV).

- WDS:
  - High spatial resolution.
  - Superior peak resolution of elements and sensitivity of trace elements.
  - Better P/B ratio and better spectral dispersion due to crystal spectrometer.
  - Crystal dependent (5 eV).

- AES:
  - Auger peaks appear as small features on intense inelastic background.
  - P/B very small.
  - Chemical shifts.

**Diagram:**

- EDS spectra with Auger peaks and Mn K\alpha.
- WDS spectra showing high resolution.
- AES spectra with Auger peaks and chemical shifts.

**General rule:** Use line markers and display simultaneously fingerprint spectra to compare.
## Other major characteristics

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| - faster and convenient to more use than WDS | - count-rates per unit beam current for pure elements:  

For a given crystal, the efficiency decreases with increasing wavelength, since the solid angle decreases with increasing Bragg angle. | - surface analysis technique with destructive depth profiles |
| - detecton artefacts: peak broadening, escape peaks, peaks shifting... | - samples need to be small and compatible with high vacuum |
| - pulse-processing artifacts: pulse processing, sensitivity to errors in dead time | - small area analysis |
| - instrumental, chemical, and sample related factors | - nonconducting samples sometimes charge under electron beam bombardment and simply can’t be analyzed |
| - AES signals in layer-by-layer growth |

![Diagram](image)

*plots 3-5: Growth and Auger electron spectroscopy characterization of donut-shaped ZnO nanostructures, ASS, Vol.253(17)*
Questions?

plot: Oxford Instruments, nano.oxinst.com