Electron Beam Induced Excitation Methods
A. Reflection Scanning Electron Microscopy
B. Auger Electron Microscopy/Spectroscopy
C. Electron Beam Induced X-Ray Analysis
D. Electron Energy Loss Spectroscopy
E. Transmission Electron Microscopy
   a. Scanning Transmission Electron Microscopy (STEM)
   b. Conventional Transmission Electron Microscopy (TEM)
   c. Energy Filtered Electron Microscopy

Ion Beam Induced Excitation Methods
A. Particle Induced X-Ray Emission (PIXE)
B. Rutherford Backscattering Spectroscopy (RBS)
C. Secondary Ion Mass Spectrometry (SIMS)
D. Ion Induced Secondary Emission Microscopy
E. Helium Ion Microscopy
SCATTERING MECHANISMS FOR CHARACTERIZATION

1. UNSCATTERED
   $\Delta E = 0, \Delta P = 0$

2. ELASTICALLY SCATTERED
   $\Delta E \neq 0$
   $\sigma_{EL} \sim Z^{3/2}$
   $\theta_o \sim \lambda / 2 \pi a x \theta_B$

3. INELASTICALLY SCATTERED
   $\theta_E \approx \frac{\Delta E}{P_0 \nu_0}$
   $\sigma_{IN} \sim Z^{1/2}$
   $\frac{d\sigma_{IN}}{dE}$ material specific
Demonstration of the Non-Localization of Inelastic Electron Scattering

( a manifestation of the Heisenberg Uncertainty Principle)

Pt on Thin Carbon Substrate

Indium atoms on carbon

9.4 nanometers
EELS of Nucleic Acid Bases obtained Using 25keV Incident Electrons


Energy Loss Spectra of Metal Fluorides

EELS Equivalent to UV Absorption

Fig. 1 Characteristic energy loss spectra of sublimed films of the common nucleic acid bases. All spectra were taken with ~20 keV electrons using those electrons scattered into a ~1 mrad cone about zero scattering angle. The total dose per spectrum was $\leq 10^{-3}$ Coulombs/cm².

Rutherford Scattering (Coulomb scatt)

\[ E_0, M_0, \vec{p}_0, Z_0 \]

\[ \phi, \theta \]

\[ Z, M \]

\[ \frac{d\sigma}{d\Omega} \propto \left( \frac{e_2}{E_0} \right)^2 \left( \frac{Z^2}{e^2} \right)^2 \left[ \frac{4 \left( \cos \theta + \sqrt{1 - x^2 \sin^2 \theta} \right)^2}{\sin^4 \theta \sqrt{1 - x^2 \sin^2 \theta}} \right] \]

where \( x = M_0/M \) same for RBS

for electrons \( x \ll 1 \) and \( Z_0 = 1 \)

\[ \therefore \frac{d\sigma}{d\Omega} \propto \frac{e^4 Z^2}{E_0} \frac{1}{\sin^4(\theta / 2)} \]

OK for larger \( \theta \)

for electrons / Ruth Scatt \~ elastic

ie, virtually no energy loss —

\[ \Delta E_{\text{max}} \approx \frac{4}{M} \frac{Me}{E_0} \]

\[ \frac{Me}{M} = 5.16 \times 10^7 \quad \text{e.g., 100 keV electrons} \]

\[ \text{Iron, } A=55.8 \text{amu} \]

\[ \therefore \Delta E_{\text{max}} \approx 3.9 \text{ eV} \]
Correction to "Rutherford" scattering

when incident e\(^{-}\) comes close to nucleus, listh scat. or \(\Rightarrow\) probability \(\propto z^2\).

BUT, if e\(^{-}\) not so close, nuclear charge "shielded" by atomic electrons so incident e\(^{-}\) doesn' t see full Z but a \(Z_{\text{eff}} \leq Z\).

this means potential is not \(V(r) \propto \frac{Z^2}{r}\) Coulomb but rather more like \(\frac{Ze^2}{r} e^{-\frac{r}{\alpha}}\)

where \(Ze^{-\frac{r}{\alpha}}\) is like an effective nuclear charge and \(\alpha = "\text{screwing" radius}\)

there are different atomic models which take this into account.

analytic ones are approximate

1930's Lenz- Wentzel / \(\alpha = a_0 Z^{1/3}\)
1970's one arrives / \(\alpha = 0.9 a_0 Z^{-1/4}\)
both show \(\alpha \propto Z^p\)
Knock-on Damage

\[ \frac{\sigma_{\text{CRIT}}}{\sigma_{\text{EL}}} \approx \left( \frac{\Lambda}{1.1a} \right)^2 \left[ \frac{E_{\text{M}}}{E_{\text{D}}} - 1 \right] \]

Single Atom Identification in STEM

1. UNSCATTERED
\( \Delta E = 0, \Delta P = 0 \)

2. ELASTICALLY SCATTERED
\( \Delta E \approx 0 \)
\( \sigma_{EL} \approx Z^{3/2} \)
\( \theta_0 \approx \lambda / 2 \pi a \approx \theta_B \)

3. INELASTICALLY SCATTERED
\( \theta_E \approx \frac{\Delta E}{P_0 \nu_0} \)
\( \sigma_{IN} \approx Z^{1/2} \)
\( \frac{d\sigma_{IN}}{dE} \) material specific

\( I_{UN} \) vs. \( \theta \)

\( I_{EL} \) vs. \( \theta \)

\( I_{IN} \) vs. \( \theta \)

\( I_{IN}(E) \) vs. \( \Delta E \)

Crystal
STEM Imaging/EELS of individual atoms/defects
From Krivanek, et.al. Ultramicroscopy.(2102) In press
Considerations on fundamental Bre. in electron induced X-ray spectra


Evaluate using classically assume radiation emitted by a charged particle in a Coulomb collision.

QM taken into account by

- Taking particle velocity to be any before and after collision.

\[
\gamma_{\text{av}} = \left[ \frac{VE_0 + VE_x - Ex}{2m} \right]
\]

Has result:

\[
\left( \frac{dE}{d\Phi} \right)_{\text{av}} = \frac{3.2 \times 10^{-11} Z^2}{\beta^2} \ln \left( \frac{1 - (VE_0 + VE_x - Ex)^2}{Ex} \right) \ m^2 / \text{eV}
\]

The "background" for electrons

In any charged particle

\[
\left( \frac{dE}{d\Phi} \right)_{\text{av}} = \frac{3.2 \times 10^{-11} Z^2 Z_{\text{f}}^2 (Me)^2}{\beta^2} \ln \left( \frac{1}{Ex} \right)
\]

\[ Z_{\text{f}} = \text{Z of target atoms} \]
\[ Z_{\text{f}} = \text{Z of inc. particle} \]
\[ Me = \text{inc. mass} \]
\[ M = \text{mass of the incident charged particle} \]

Note: we increase by going to higher energies or by using incident particles of higher mass than Mo next!
what is the max weak we can detect with Xrays //
charged particle induced Xrays

peak signal (cts) = \( S_p \) = \( N_a J_{\alpha} Y_{\alpha} F_{\alpha} \times \frac{\text{count time}}{\text{from beam type A}} \)

\[ S_p = \frac{M_{\alpha}}{A_{\alpha} m_p} J_{\alpha} Y_{\alpha} F_{\alpha} \times \frac{\text{peak time}}{\text{at wt}} \]

\[ \text{total mass} \]

\[ \text{atom mass} \]

\[ \text{avg A of sample} \]

\[ \text{energy balance} \]

log signal (cts) = \( S_{\text{log}} \) = \( \frac{M_T}{A_{\text{comb}}} J_1 \left[ \frac{\text{d}E}{\text{d}E_{\text{br}}} \right] - F \times \frac{\text{peak time}}{\text{ Brigham Y=1 why?}} \)

- Conditions for detection

\[ P_A = \sqrt{N_p \text{peak}_{\text{comb}}} \]

\[ 1 \times \frac{S}{N} = \sqrt{N} \text{ Poisson stats} \]

- Contrast factor - from Rose.

- Take the two eqns: 1st for \( M_{\alpha} \), 2nd for \( M_T \)
detected.

\[ \text{get mass fraction} = MF = \frac{M_{\alpha}}{M_T} = k \frac{A_{\alpha}}{A_{\text{comb}}} \left[ \frac{\text{d}E}{\text{d}E_{\text{br}}} \right] \frac{\text{d}E_{\text{br}}}{\text{J}} \]

- 2 pts to decrease MF

1. increase \( Y_{\alpha} F \)
2. decrease \( \frac{\text{d}E}{\text{d}E_{\text{br}}} \)
3. increase y
4. decrease \( \text{d}E \)
Detectable Mass Fraction

X-ray detection, EDX

Detectable mass fraction, MF

$E_0 = 190\text{ keV}, \ \Delta E = 150\text{ eV}, \ \tau = 100\text{ sec}, \ k = 3$

$\Box \ d_g = 1\text{ nm}, \ \Box \ d_g = 10\text{ nm}$

$T_{\text{substrate}} = 100\text{ nm}$
Minimum Detectable Concentration, EELS

![Graph showing minimum detectable concentration as a function of atomic number.]

**Figure 3.**

Detectable mass fraction \( MF = K \rho \left[ \frac{m_p e}{A M \varepsilon} \right]^{1/2} \frac{e^{nt/\sqrt{2}}}{\sigma_0} \)

We assume 100 keV incident electrons. Sample is 1000 Å thick.

All curves assume \( K = 3, J_b = 1.27 \times 10^5 \text{Amps/cm}^2, (J_b = 10^{-9} \text{Amps, d_b = 10Å}) \) and \( T = 100 \text{ SEC.} \)
so what strategy to reduce min. det. conc.

- Note \( M_{rJ} = \frac{\pi d_e^2}{4} (\frac{I_p}{\pi d_e^2}) \)
  
  \( = \pi I_p \) — decreasing beam size doesn’t reduce MF
  
  but increasing \( I_p \) does reduce MF.

- Increasing the counting times, \( T \), reduces MF

- \( \frac{\Delta E}{E} \) reduction helps — depends on detector

- Increasing \( \gamma_0 \) helps — depends on process we choose

- \( \frac{dS}{dE} \propto \frac{1}{\beta^2 (\text{Mun})^2} \) so increasing the velocity

  of the particle or increasing its Mun. helps also

- we will discuss all of these —

  1. detectors

  2. \( \gamma_0 \rightarrow \) if you detect energy not electrons

    rather than x-rays, \( \gamma_0 = 1 > \text{Mun} \)

  3. If you use protons rather than Mun. \( \gamma \) so MF <

  4. Higher energies help somewhat since \( \frac{dS}{dE} \propto \frac{1}{\beta^2} \) but

    so does x-ray — so not so big an effect
minimum detectable concentration for proton induced x-ray fluorescence each solid line corresponds to the proton energy in MeV.

The detectable weight concentration of a trace element of atomic number $Z$ in a 0.1 mg/cm$^2$ carbon matrix.

The concentration calculated assumes peak counts = $2\sqrt{2} \times$ background count.

The solid angle that the Si(Li) detector subtends is $\Omega = 0.003 \times 4\pi$ ster. We assume 100% detector efficiency.

The incident proton charge is 10 nC and the signal detailed to X-rays.

Most of the experimental facilities of our laboratory are based on a 5 MV Van de Graaff (VdG) electrostatic accelerator. VdG provides energetic ions (H+, D+, He+, etc.) for ion beam analysis, physical experiments, as well as for the modification and testing of materials.

http://iba.atomki.hu/facilities.html
PIXE Applications and Theory

Elemental Analysis Incorporated, utilizing Proton Induced X-ray Emission (PIXE), provides a non-destructive, simultaneous analysis for the 72 inorganic elements from Sodium through Uranium on the Periodic Table for solid, liquid, and thin film (i.e. aerosol filter) samples. The PIXE technique offers the advantage of analysis, without the necessity for time consuming digestion, thereby minimizing the potential for error resulting from sample preparation.

Sample Types

Solids – such as plastics, papers or metals, are analyzed “as received,” while powdered materials, such as fly ash, activated carbon, catalysts, and corrosion products, are ground to 200 mesh or finer and pressed into pellets for analysis.

Liquid – samples, such as oils, process waters, and solutions, are analyzed using a plastic cup of either 8 mL or 3 mL in capacity with a 0.3 mil Kapton front surface window, and can be analyzed “as received” by this method without modification. However, some liquids (i.e. highly caustic or highly acidic) may require predilution or neutralization before analysis.
Stopping-Power and Range Tables for Electrons, Protons, and Helium Ions

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Abstract:
The databases ESTAR, PSTAR, and ASTAR calculate stopping-power and range tables for electrons, protons, or helium ions, according to methods described in ICRU Reports 37 and 49. Stopping-power and range tables can be calculated for electrons in any user-specified material and for protons and helium ions in 74 materials.

Contents:
1. Introduction
2. ESTAR: Stopping Powers and Ranges for Electrons
3. PSTAR and ASTAR: for Protons and Helium Ions (alpha particles)
   References
   Appendix: Significance of Calculated Quantities

This work was supported in part by the Department of Energy, Office of Health and Environmental Research, Washington, D.C. 20585; and by NIST's Systems Integration for Manufacturing Applications (SIMA) Program.
Micro-PIXE analysis of an Egyptian Papyrus

Identification of the pigments used for the "Book of the Dead"

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View of the external microprobe set-up with the papyrus in place

The Papyrus KM 21933 consists of hieroglyphic text ended by a painted vignette. It forms the right end of a "Book of the Dead" from the Theban 19th Dynasty (c.1295– 1186 B.C.). This name is given to religious funerary texts and spells for protection and guidance of the deceased entering the afterlife. Probably discovered in the 1820’s, it was acquired in Berlin in 1912 by The Kulturen Museum in Lund, Sweden.
HARVARD PIXE SYSTEM
Particle Accelerators
in Art & Archaeology

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www.presid.infn.it/er/er04fazio.ppt

Erice, April 17, 2004
PIXE analysis of ancient manuscripts

(INFN Firenze, Biblioteca Vaticana, Biblioteca Laurenziana)

Detecting which pigments were employed provides important art-historical information, both about general trends and specifically about the analysed work. More or less precious materials ↔ symbolic value of the text. Trade routes of raw material import from countries far away. Added or restored parts.

External-beam PIXE analysis of the frontispiece of Pl.16,22, from Biblioteca Laurenziana in Florence
differential PIXE to discriminate the contributions of different layers

\[ E_1 < E_2 < E_3 \]

+ simultaneous use of PIGE to detect light elements