Ion Scattering Spectroscopy

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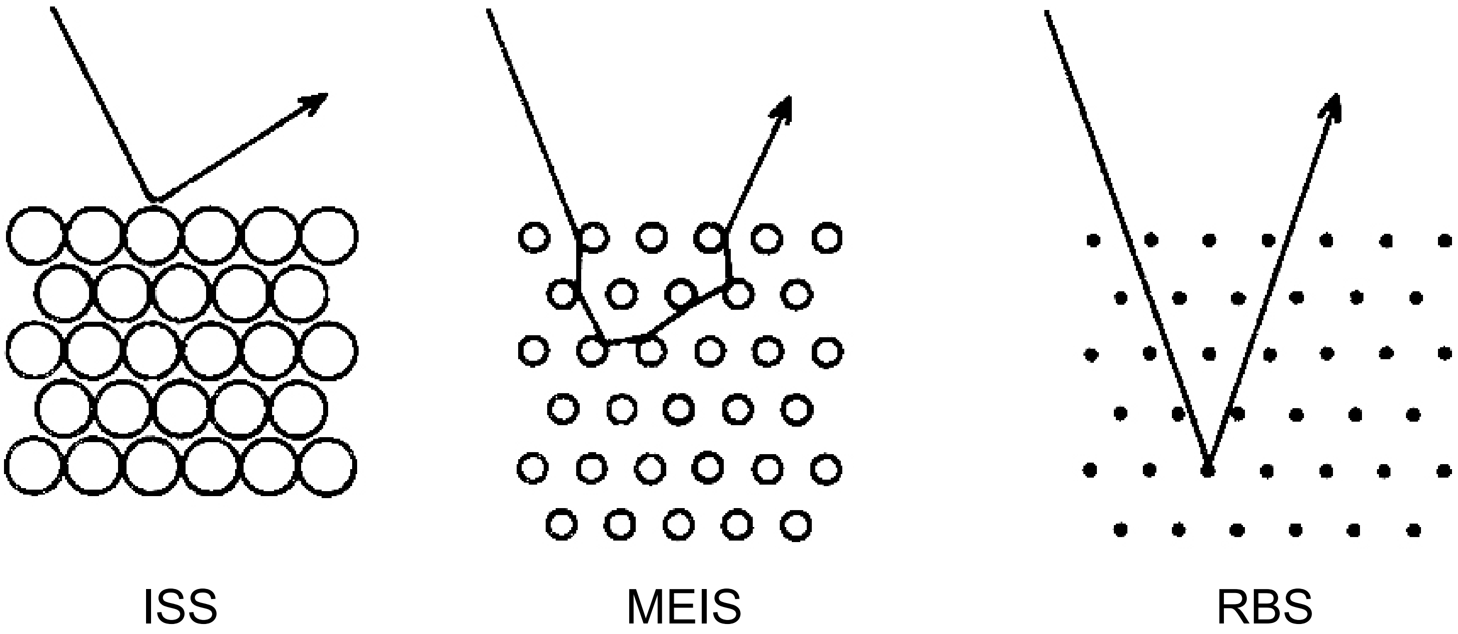
Ion spectroscopies

1. **Ion scattering (elastic interaction)**
   - Low-energy ion scattering (ISS or LEIS, ~500 eV — some keV)
   - Medium-energy ion scattering (MEIS, 20 — 200 keV)
   - High-energy or Rutherford backscattering spectroscopy (RBS, ~MeV)
   - Elastic recoil detection analysis (ERD, keV — MeV)

2. **Nuclear reaction analysis (NRA)**
   - Uses nuclear reactions (some 100 keV — MeV)

3. **Secondary ion mass spectroscopy**
   - Detection of sputtered ions (SIMS) or neutral particles (SNMS) through mass analysis

Ion scattering

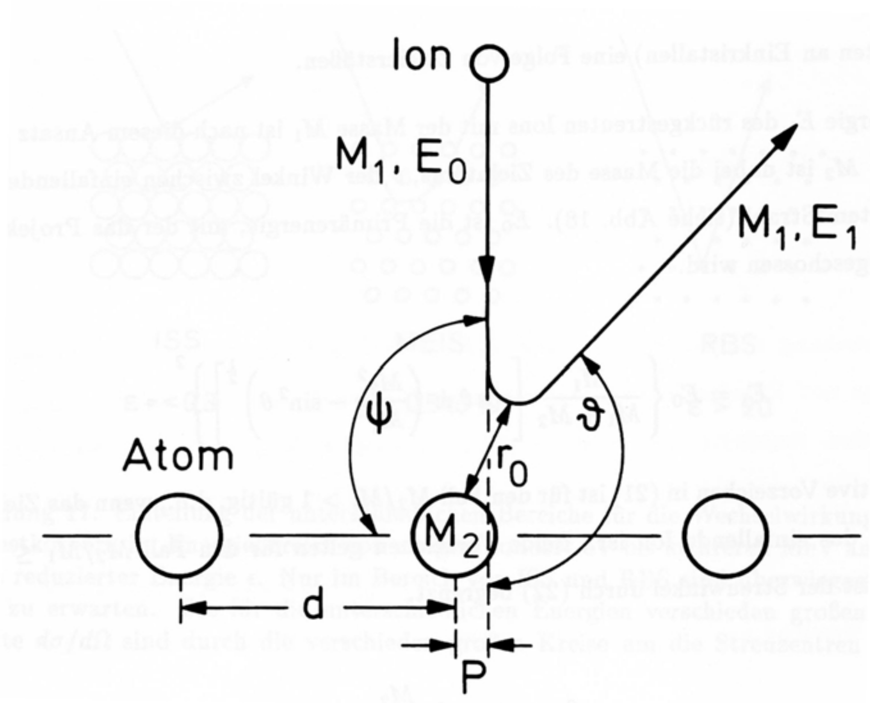


ISS, RBS: binary collision

MEIS: multiple collisions, inelastic energy losses

for surface analysis: ISS (first atomic layer) and RBS (surface-near zone)

Kinematics of binary collision

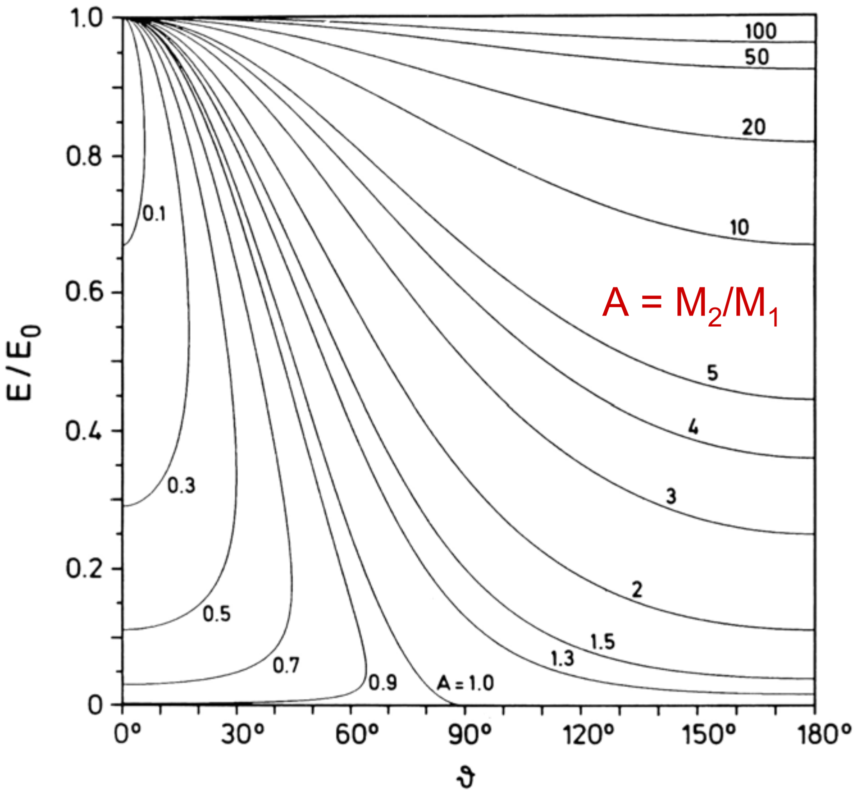


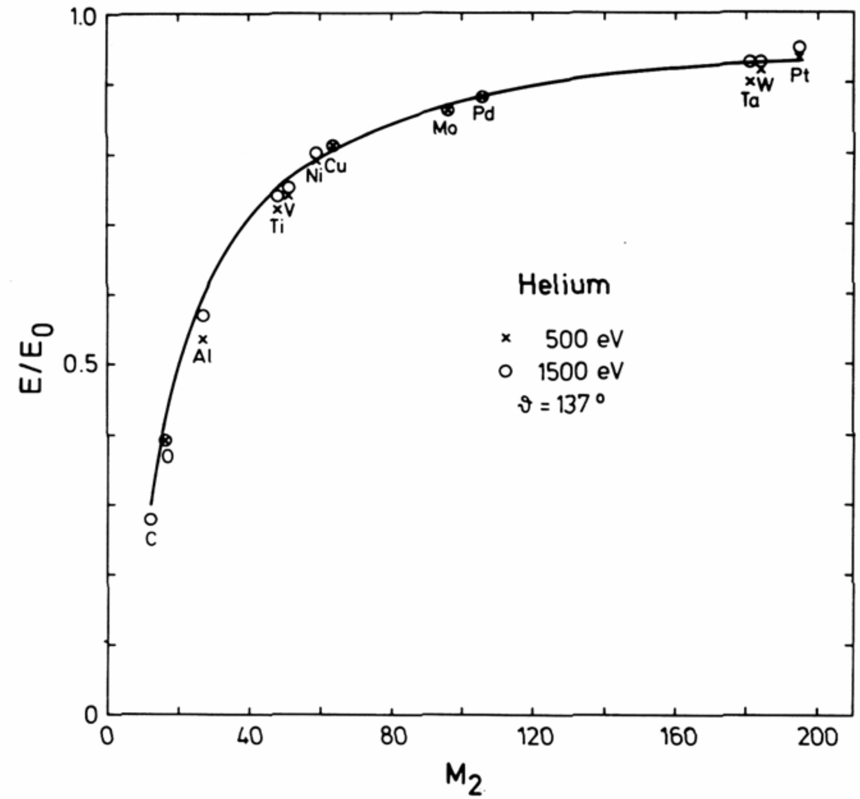
$$E_1 = K \cdot E_0$$

$$K = \frac{1}{1+(M_2/M_1)}\left\{\cos\vartheta \pm \left[\left(\frac{M_2}{M_1}\right)^2 - \sin^2\vartheta\right]^{\frac{1}{2}}\right\}^2$$

- Interaction time: 10^{-15}-10^{-16} s (ISS; RBS even shorter!). Compare to lattice vibrations: ~10^{-13} s.
- Conservation of energy and momentum: elastic scattering
- E/E_0 is a function of the scattering angle θ and of the mass ratio $A = M_2/M_1$
- An energy spectrum of the backscattered ions M_1 can be converted directly into a mass spectrum.

Mass resolution



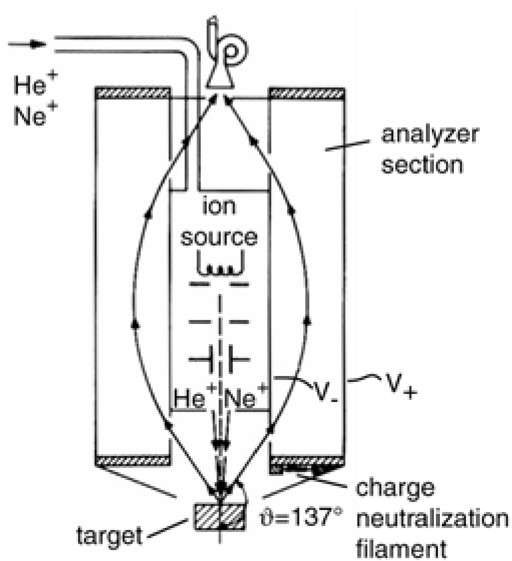


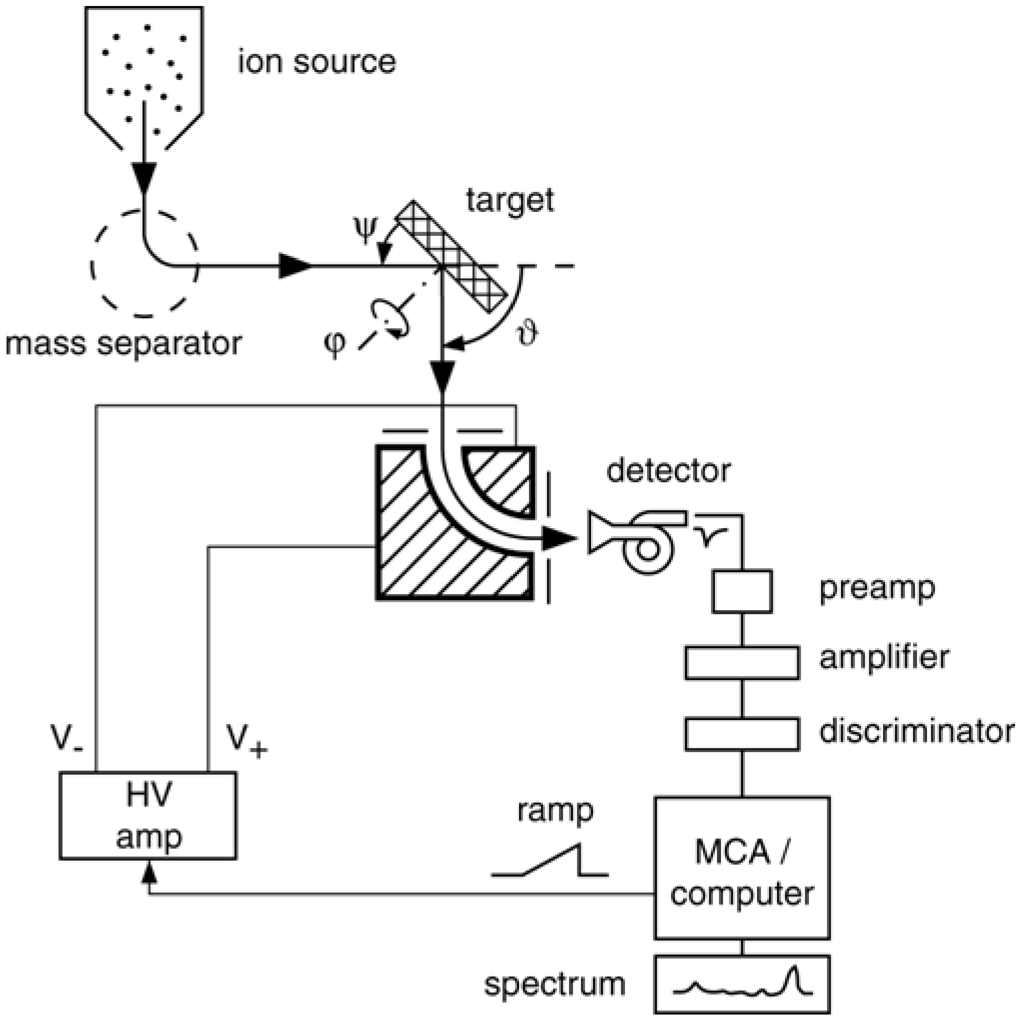
- For large scattering angles: good mass resolution, if A small (use He as projectile for light elements!)
- Bad mass resolution for heavy elements

ISS experimental setup

Vacuum:

1 ML sensitivity → ultrahigh vacuum (below 10^{-9} mbar) necessary!

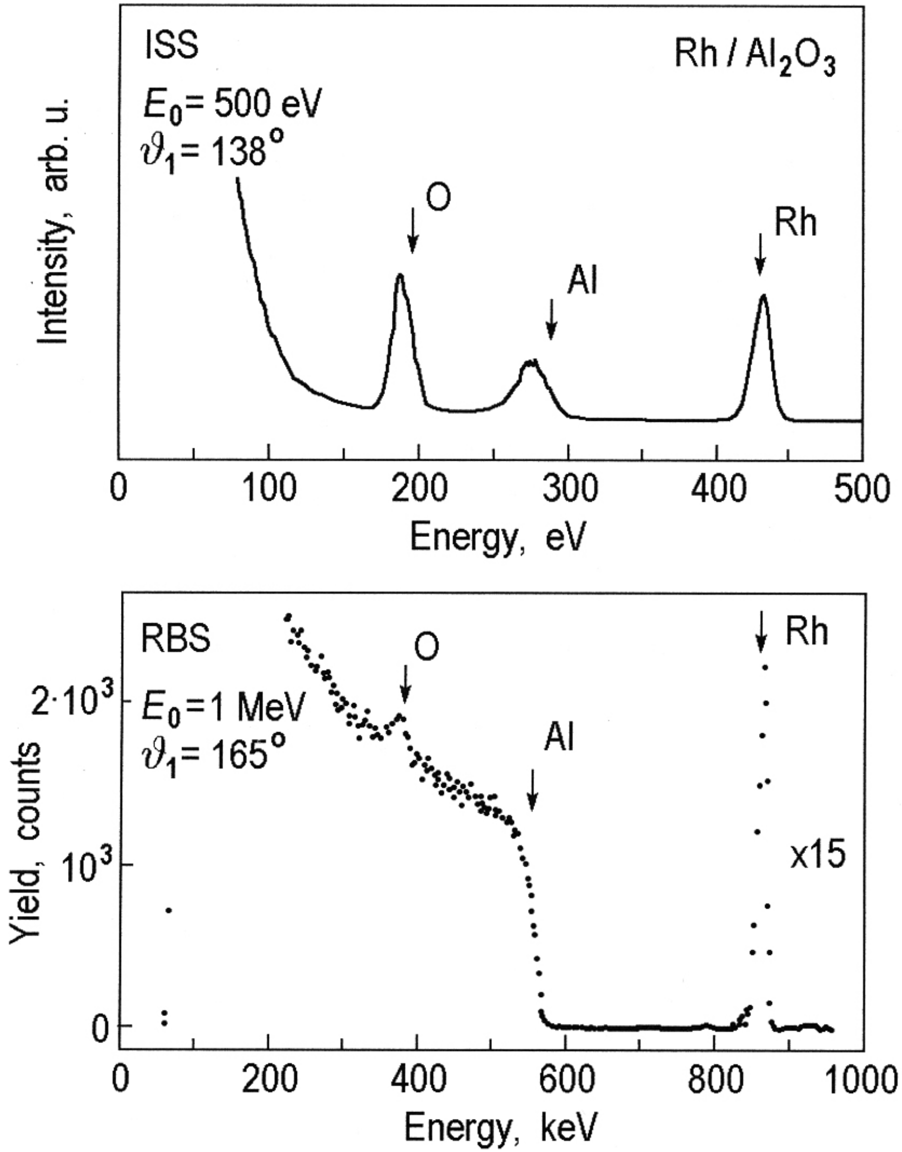




Energy analyzer:

cylindrical mirror analyzer (CMA)

ISS and RBS: binary collision



1 ML Rh / Al_2O_3

Simple concept of energy and momentum conservation is valid over many orders of magnitude of primary kinetic energy:

ISS: 500 eV He^+

RBS: 1 MeV He^+

ISS: surface sensitivity

Noble gas ions:

ISS is sensitive for the first atomic layer when backscattered ions are detected!

Reason: large ion neutralization probability

Typical ion survival probabilities for scattering at metal surfaces
(E_0 = 1 keV, θ = 60°):

Scattering in	He^+	Ne^+	Li^+	Na^+
first layer	< 0.1	single: < 0.04 double: < $4x10^{-3}$	0.9-1	0.8
deeper layers	< $3x10^{-3}$	< $4x10^{-3}$	0.9-1	0.8

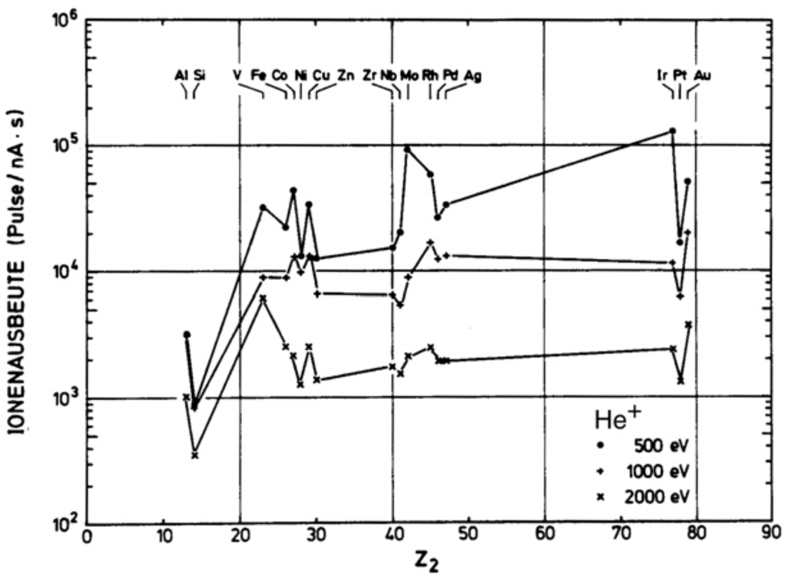
ISS: neutralization

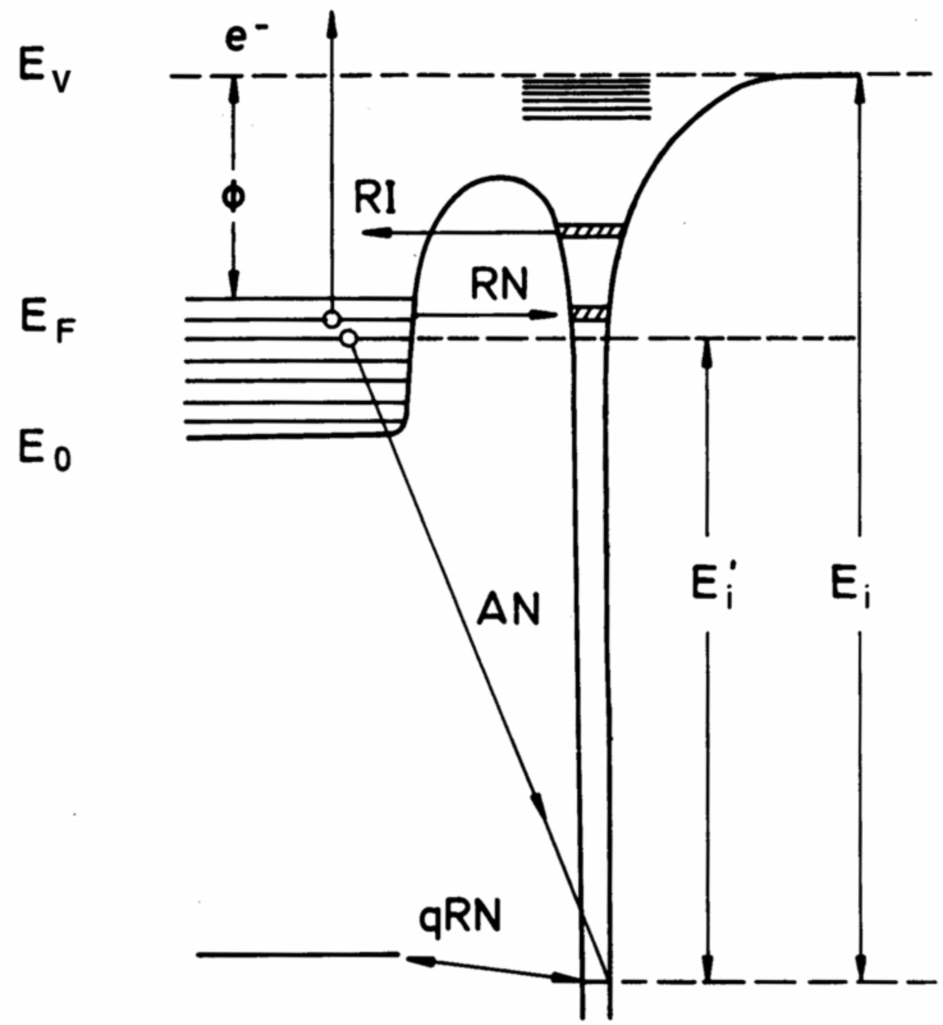
Charge transfer processes:

AN: Auger neutralization

RN, RI: resonance neutralisation / ionisation

qRN: quasi-resonant neutralization



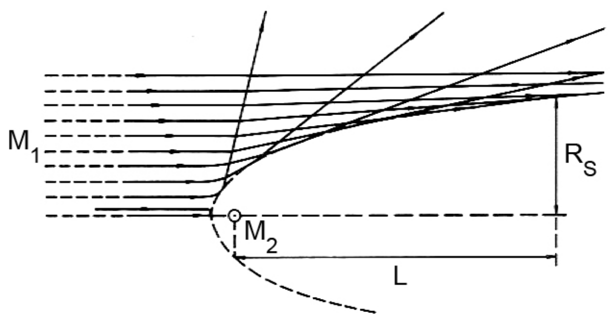


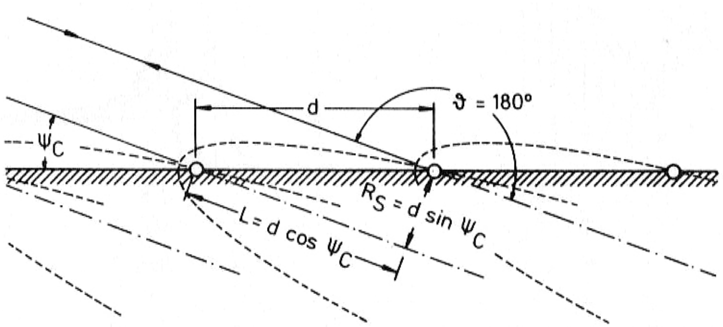
Quantification of ISS difficult, „matrix effects“

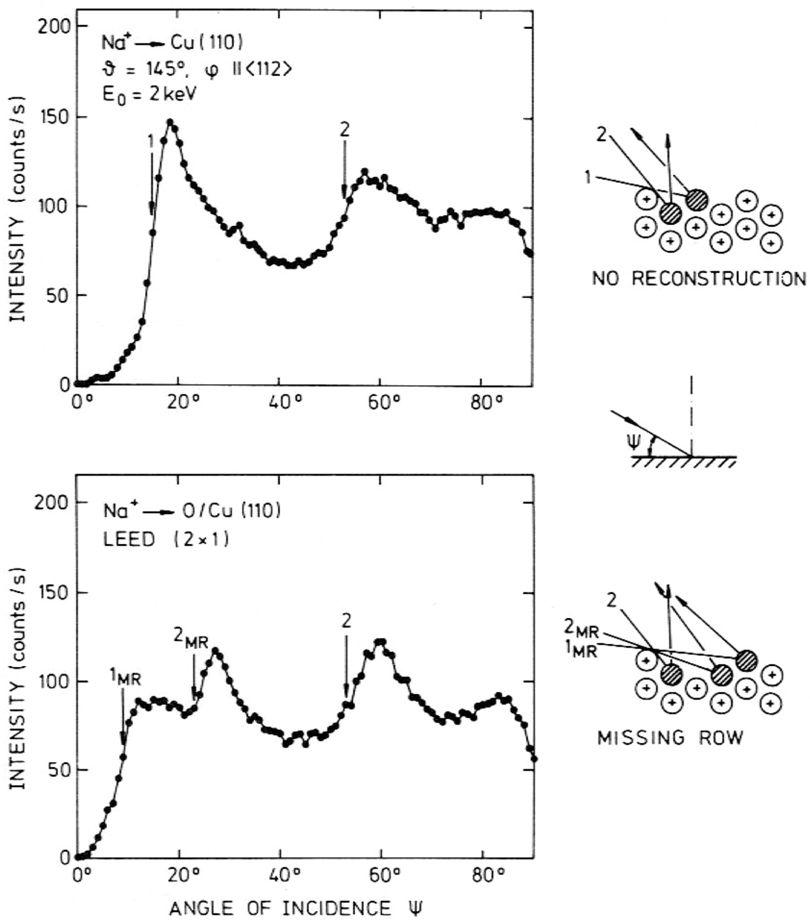
Structure analysis by ISS

ICISS: Impact Collision Ion-Scattering Spectroscopy

- ➢well-ordered surface (single crystals)
- ➢shadow-cone concept
- ➢use of noble gas or alkali ions (deeper layers)



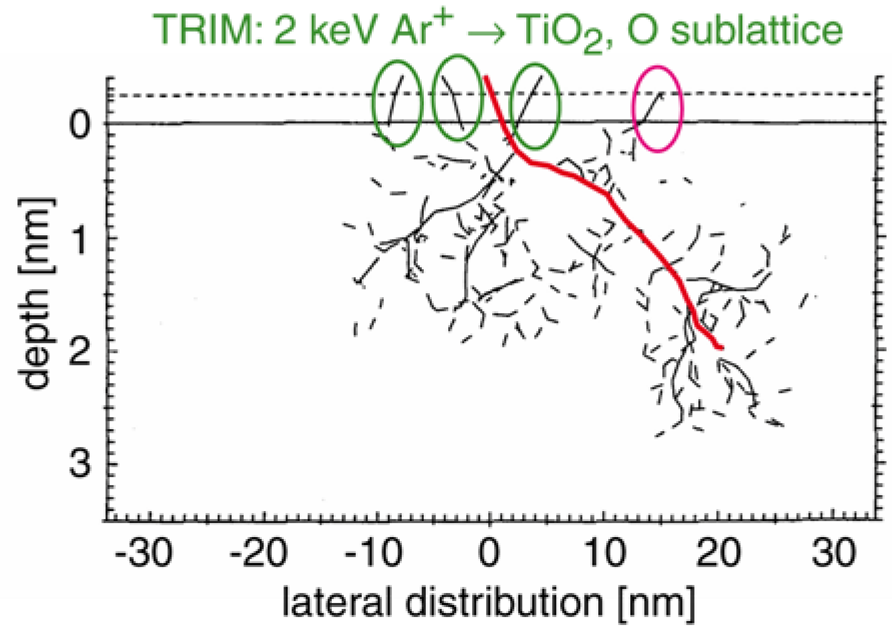


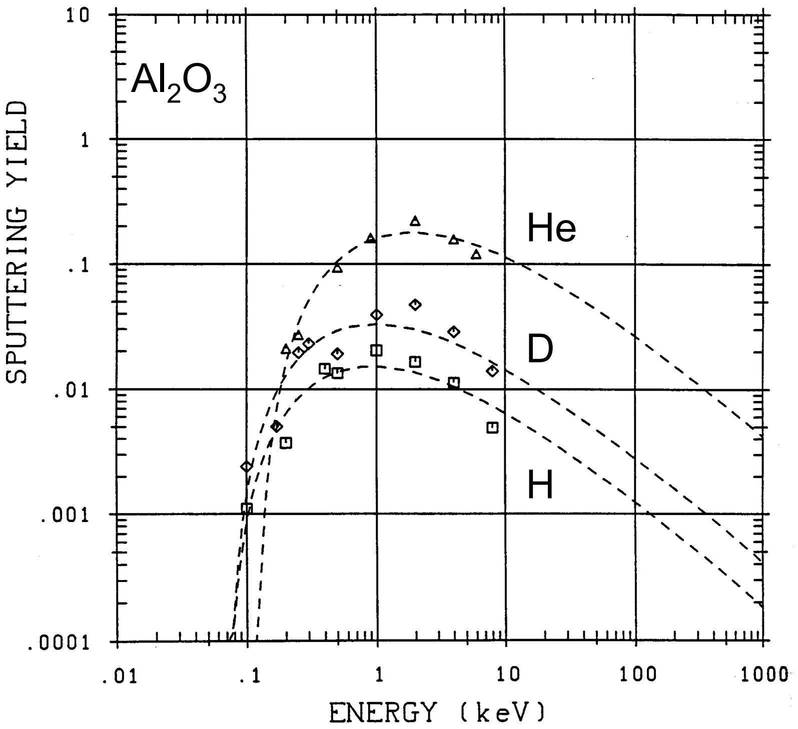


H. Niehus, G. Comsa, Surf. Sci. 140 (1984) 18

Sputtering

In addition to backscattering: **collision cascade** in near-surface zone, removal of atoms



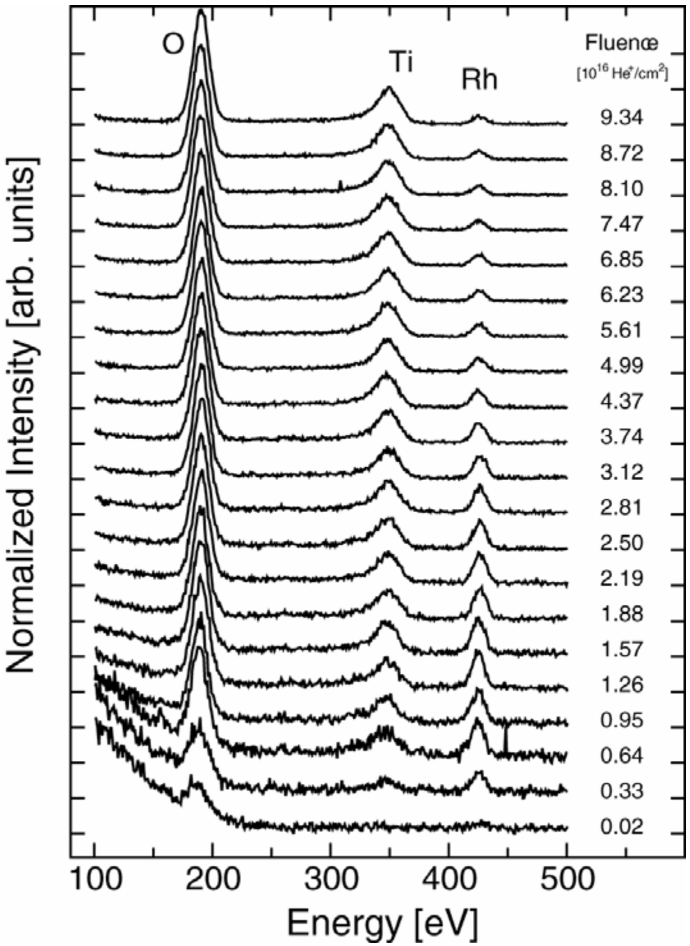


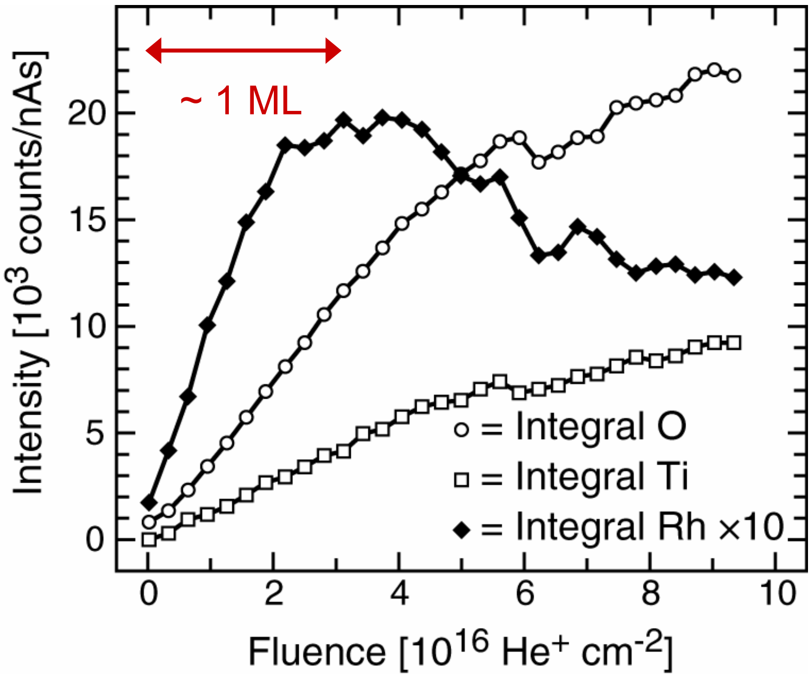
Sputtering yield:

$$Y = \frac{\text{number of sputtered atoms}}{\text{number of incoming projectiles}}$$

ISS: model catalyst

1 ML Rh / TiO_2 500 eV He^+ θ=137°

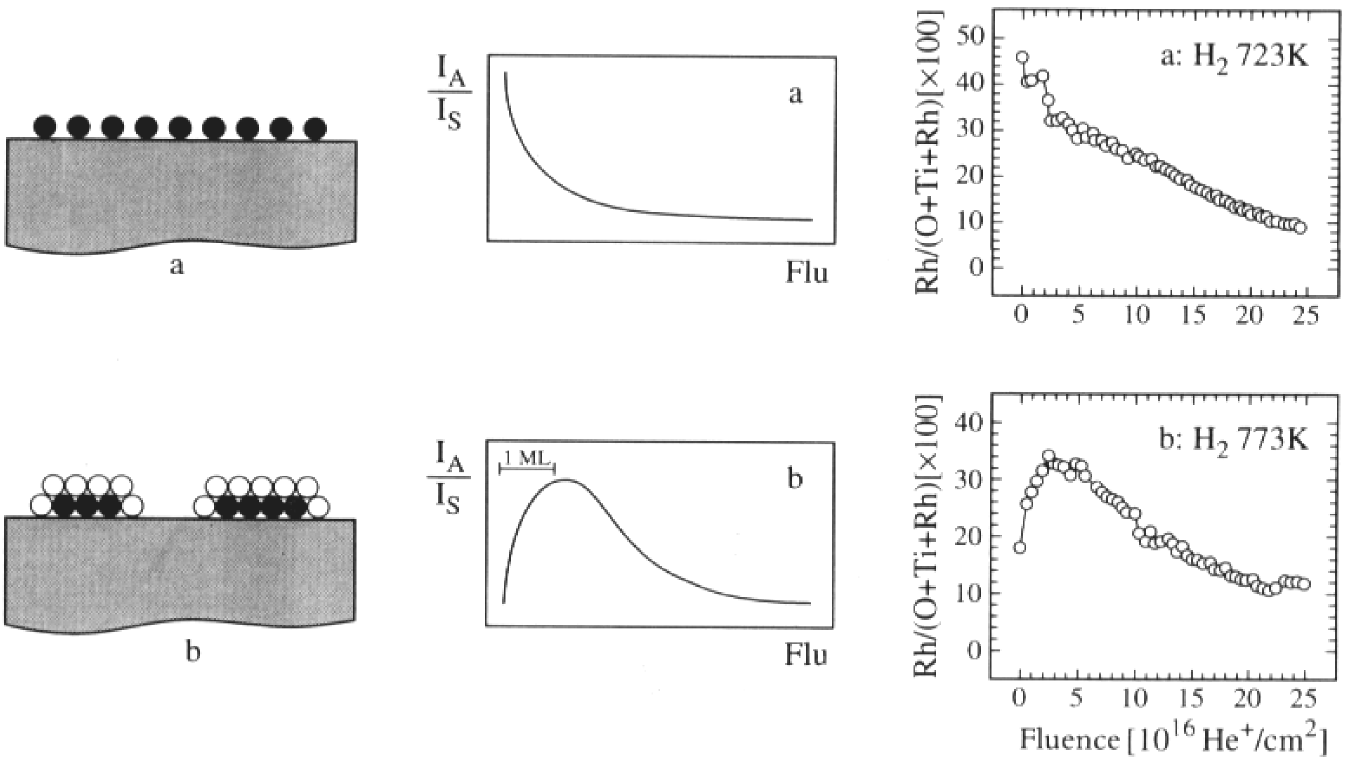




- Depth profile with very good depth resolution
- Limit: ion beam effects!

SMSI: Strong Metal-Support Interaction

1 ML Rh / TiO_2 500 eV He^+ θ=137°



as deposited

encapsulated

- ISS provides direct proof for encapsulation

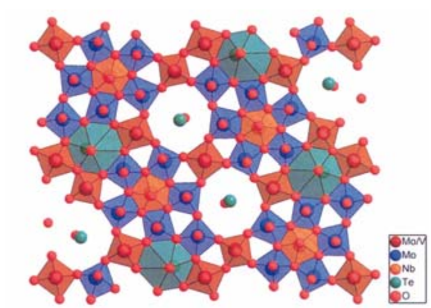
Active surface vs. bulk composition

Mo-based mixed oxide catalyst for selective oxidation reactions

- composition of active surface?
- ISS analysis, comparison to bulk composition

M1 = $Mo_1V_{0.15}Te_{0.12}Nb_{0.128}O_{3.7}$

$Mo_{7.8}V_{1.2}Te_{0.937}Nb_1O_{28.9}$



Nominal composition: $Mo_1V_{0.3}Te_{0.23}Nb_{0.13}$

M1 composition*: $Mo_1V_{0.15}Te_{0.12}Nb_{0.13}$

method	*Mo*	*V*	*Te*	*Nb*
LEIS reference M1	1.00	0.25	0.15	0.22
LEIS silylated M1	-	-	-	-
LEIS, silylated M1, 10% new surface after grinding	1.00	0.27	0.10	0.09
SEM / EDX silylated	1.00	0.26	0.10	0.15
SEM / EDX silylated, ground	1.00	0.26	0.09	0.16

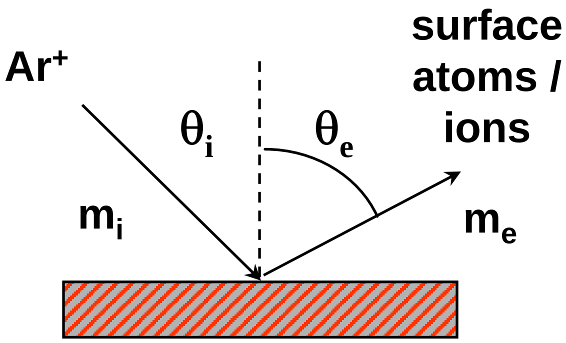
*P. De Santo et al., Z. Kristallogr. **219** (2004) 152.

- ISS (=LEIS): first layer enriched in Te and Nb
- catalytic properties determined by an adlayer on M1 substrate

Trunschke, Schlögl, Guliants, Knoester, Brongersma, 232nd ACS Meeting (2006)

Secondary ion mass spectrometry (SIMS)

Principle



Extremely sensitive (ppm to ppb), quantification problematic (pronounced matrix effects)

Static SIMS ↔ Dynamic SIMS

Excitation

- Noble gas ions (Ar^+, 0.5 - 5 keV)

Detector

- Mass spectrometer

Emittied surface species

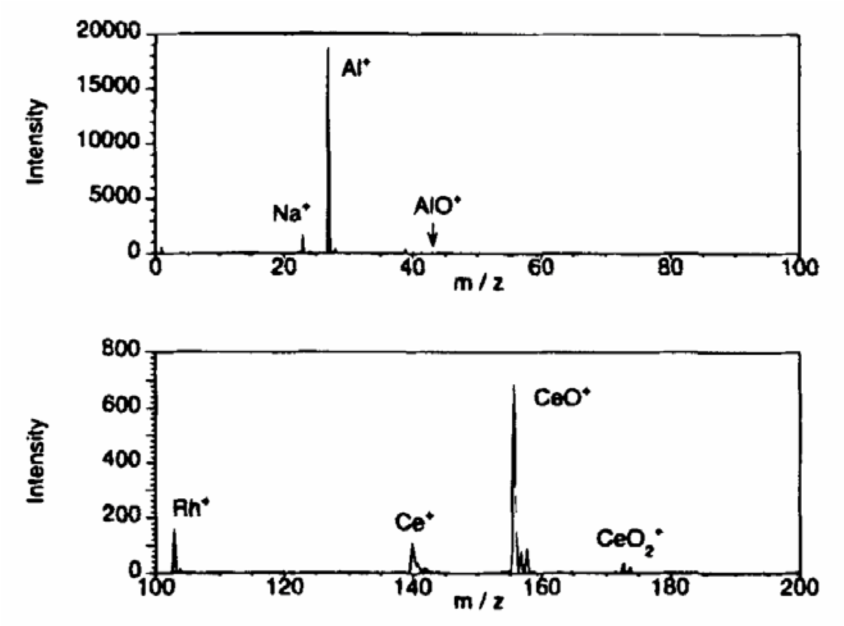
- Ions
- Molecular fragments
- Clusters of surface atoms and ions
- Neutrals (SNMS)

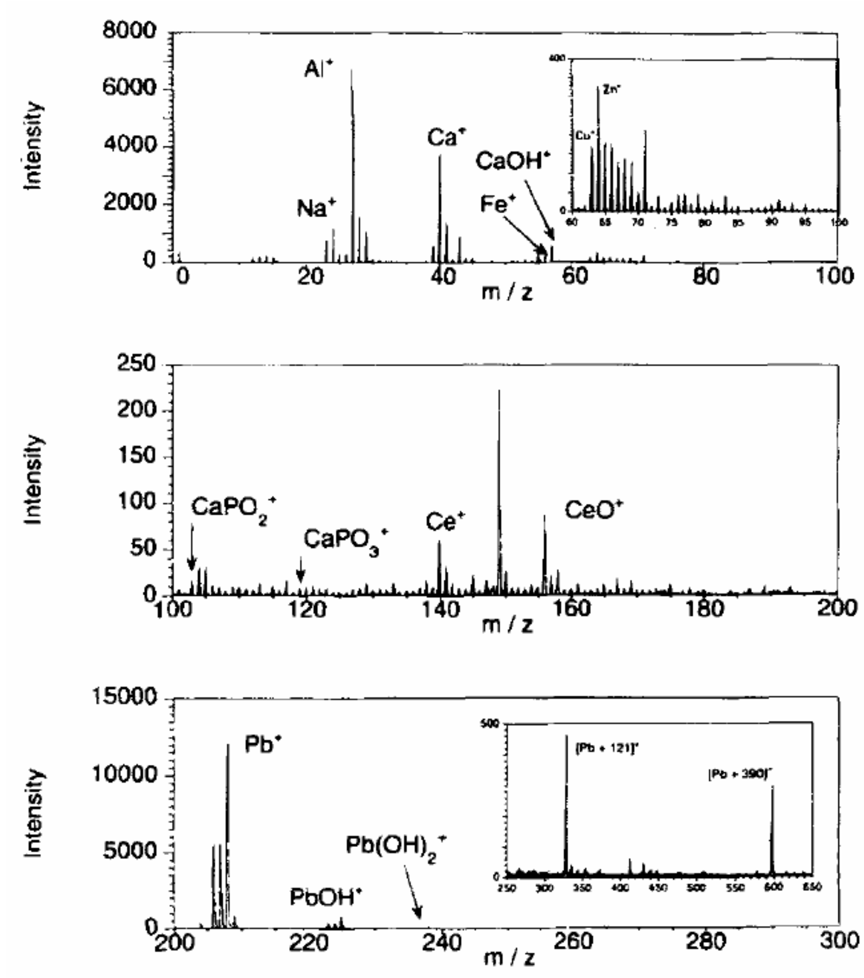
Intensity

$I \propto Q$

Q: Probability for formation of secondary ions, depends very sensitively on matrix.

SIMS – Poisoning of a 3-way catalytic converter





new catalytic converter:

no phosphates, lead compounds

after 121000 km:

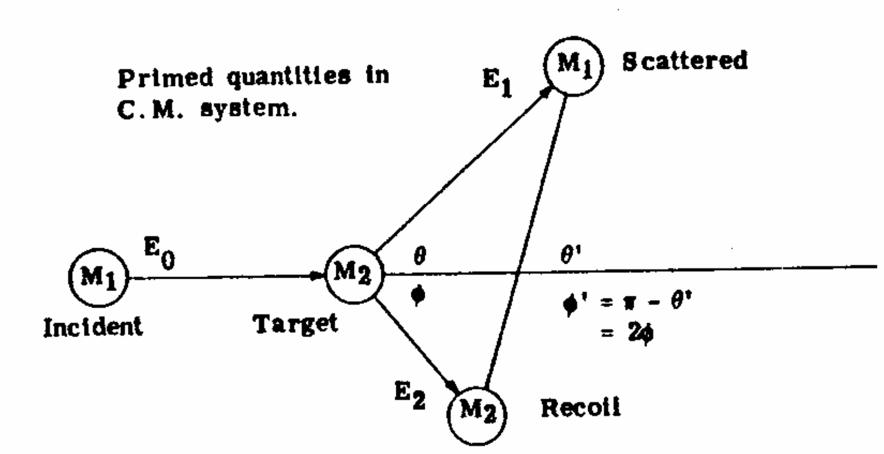
Poisoning by phosphates and lead compounds, less CeO_x due to sintering

Oakes and Vickerman, Surf. Interface Anal. 24 (1996) 695

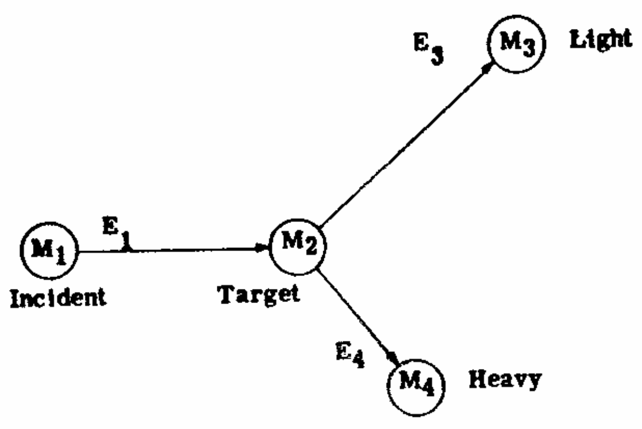
Accelerator-based techniques

RBS	Rutherford Backscattering Spectrometry
NRA	Nuclear Reaction Analysis
ERD	Elastic Recoil Detection Analysis

primary energy: ~100 keV up to several MeV



RBS, ERD



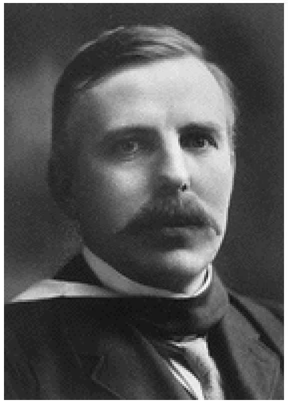
NRA

RBS

Sir Ernest Rutherford (1871 - 1937)

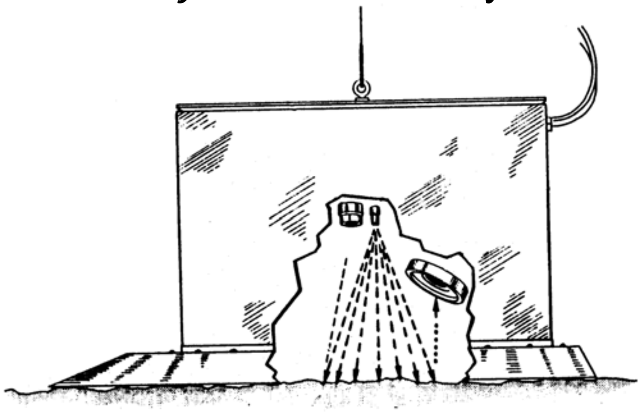
- 1911: scattering experiments ^{4}He $\rightarrow$ Au (foil)

  $\Rightarrow$ Discovery of atomic structure (nucleus, electrons)



- 1967: RBS on the moon

  Surveyor V lands softly on the moon



- today: ion accelerator!

RBS: Quantification and sensitivity

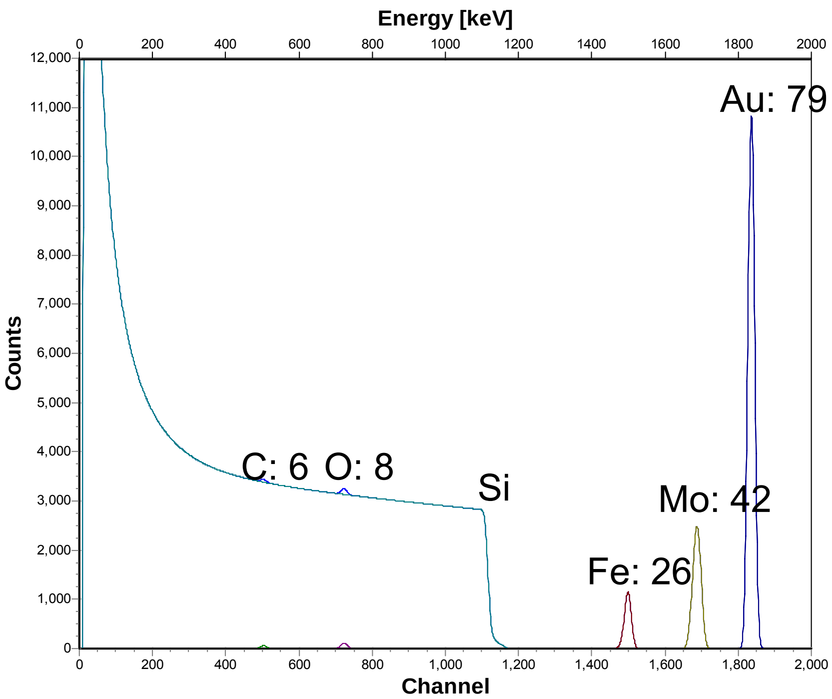
Scattering cross section

- Coulomb interaction between projectile and scattering atom unscreened Coulomb potential!

$$\sigma_R \propto \frac{Z_1^2 Z_2^2}{E^2}$$

Sensitivity increases with:

- increasing atomic number of projectile and scattering atom (Z_1 and Z_2)
- decreasing energy E



2 MeV ^{4}He, θ = 165°

Sample: C, O, Fe, Mo, Au, each 3×10^{16} atoms/cm^2 on Si substrate

⇒ more sensitive for heavy elements $\propto Z_2^2$

⇒ good: heavy elements on light substrates

⇒ bad: light elements on heavy substrates

RBS: Information on depth distribution

Stopping power

- electronic energy loss
- nuclear energy loss

$$S = -\frac{dE}{dx}\frac{1}{n} \qquad unit: \frac{\text{eV}}{\text{atoms cm}^{-2}}$$

Bragg's Rule: Compounds

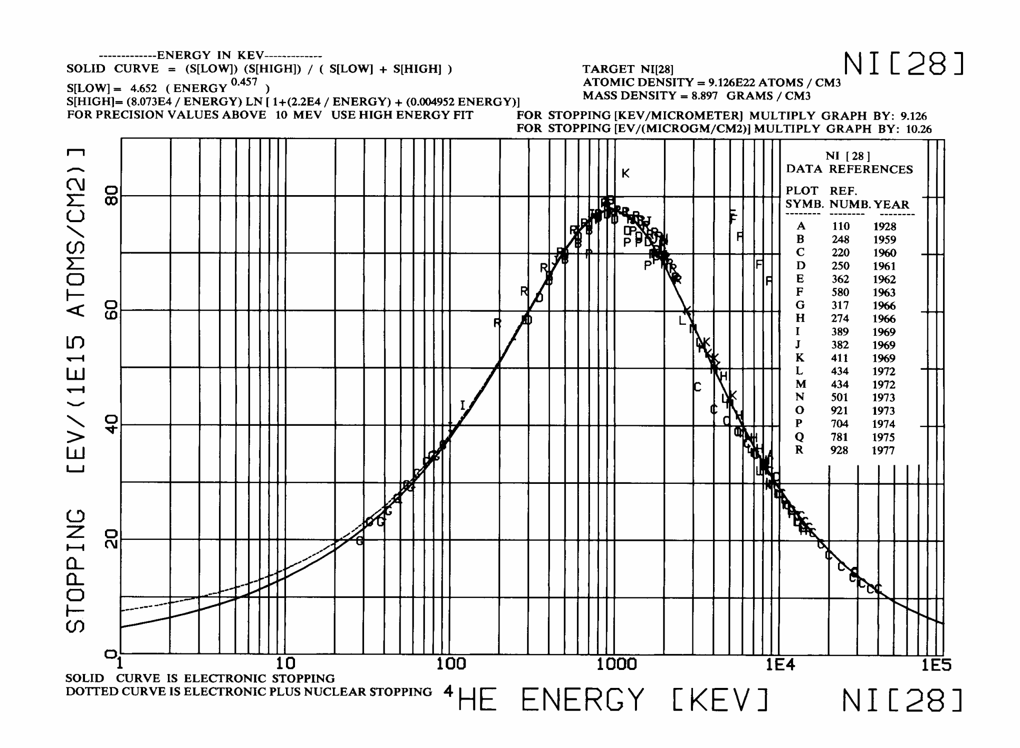
- exact: metallic alloys
- approximate (up to 20%):
  hydrocarbons, oxides,nitrides, …

Compound A_mB_n

S_A is stopping power of element A

S_B is stopping power of element B

$$S_{AB} = m\, S_A + n\, S_B$$



J.F. Ziegler, Helium - Stopping Powers and Ranges in All Elements, Vol. 4, Pergamon Press, 1977

Impregnation of MoO_3/Al_2O_3 model catalysts

Preparation

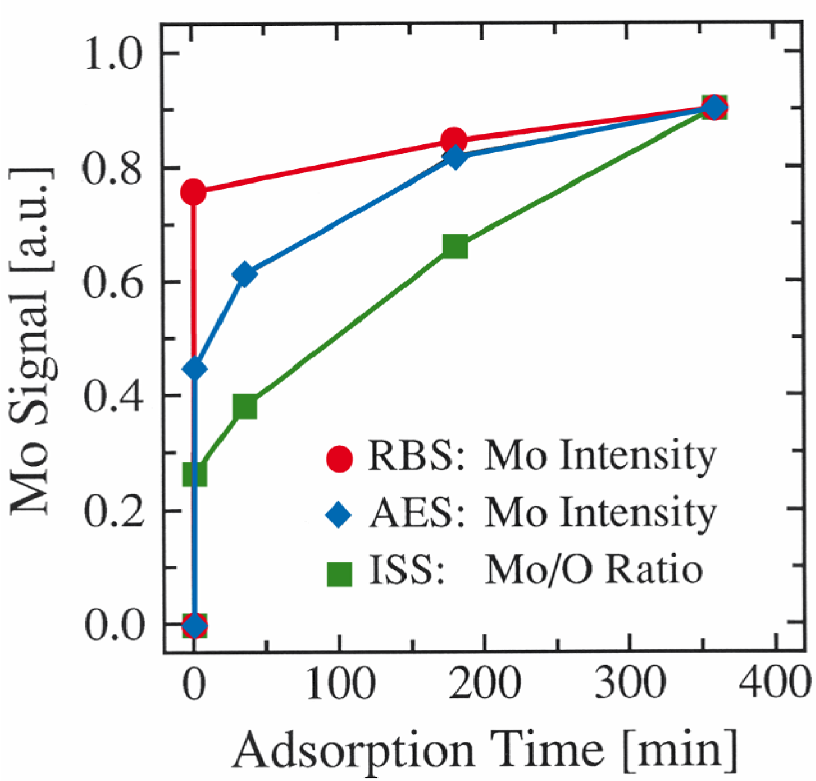
- anodic oxidation of Al foil
- impregnation of oxide with ammonium heptamolybdate solution

Analysis

- Mo signal from techniques with different depth information:
  RBS: ~50 ML
  AES: ~5 ML
  ISS: 1 ML

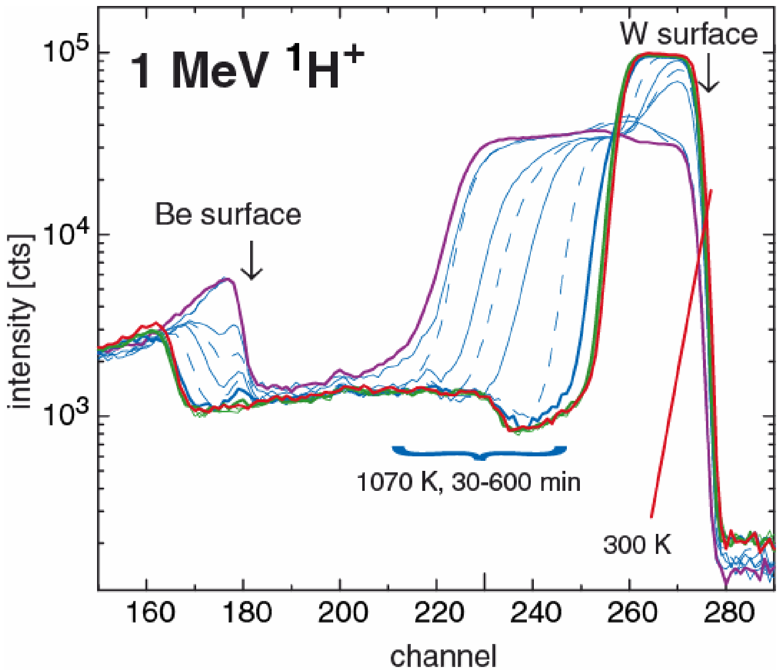
Mechanism

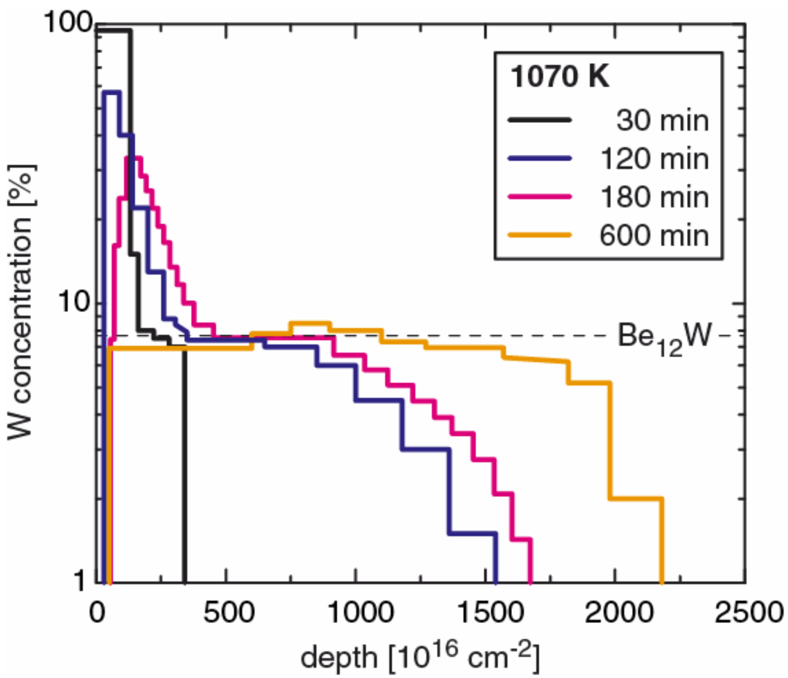
- pore filling (RBS) in less than 1 min
- molybdate surface adsorption within hours (ISS)



RBS: Example depth profile

235 nm W on Be, alloy formation during annealing





depth distribution:

- determination of depth distribution by comparison of measured with simulated spectra
- consideration of kinematics, scattering cross section, and stopping power

NRA: Nuclear reaction analysis

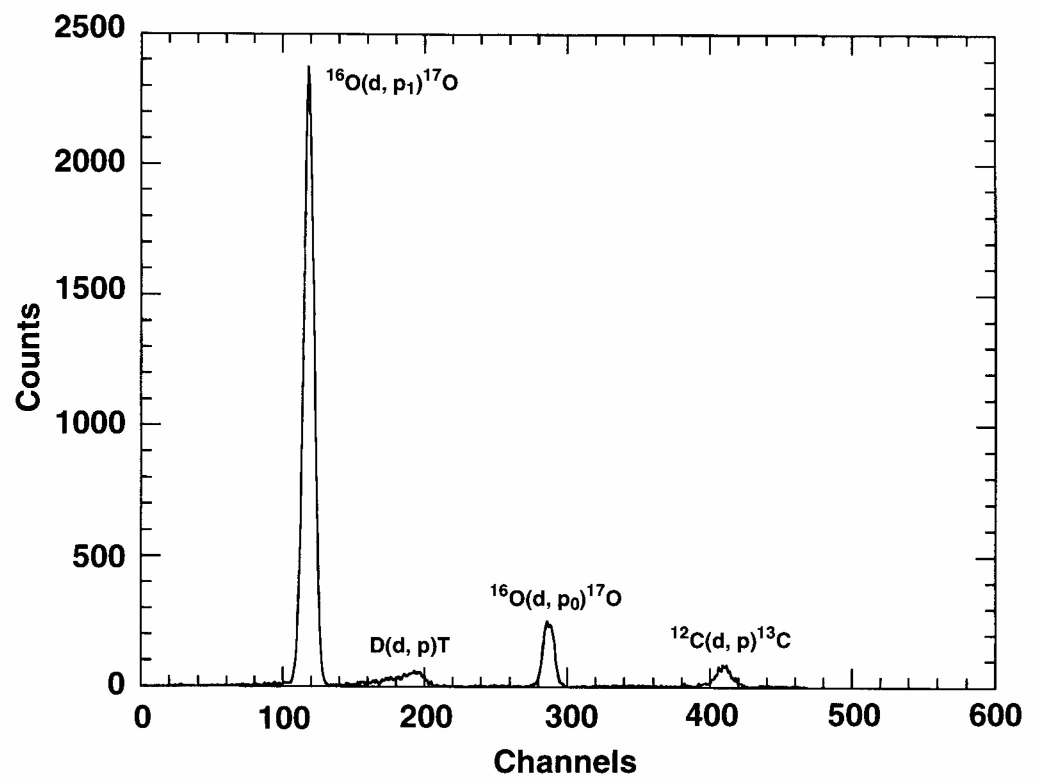
Advantage:

- sensitive for light elements
- signal at large channel numbers/energies in spectrum: no background!

Reactions:

- ^{3}He induced:
  $D(^{3}He,p)^{4}He$
  $^{9}Be(^{3}He,p)^{11}B$
  $^{12}C(^{3}He,p)^{14}N$
- proton induced:
  $^{7}Li(p,\alpha)^{4}He$
  $^{11}B(p,\alpha)^{8}Be$
  $^{18}O(p,\alpha)^{15}N$
- deuterium induced:
  $^{12}C(d,p)^{13}C$
  $^{14}N(d,p_{0-6})^{15}N$
  $^{16}O(d,p_{0,1})^{17}O$

Example:
834 keV deuterium on SiO_2/Si
θ = 135°, 12 µm Mylar absorber



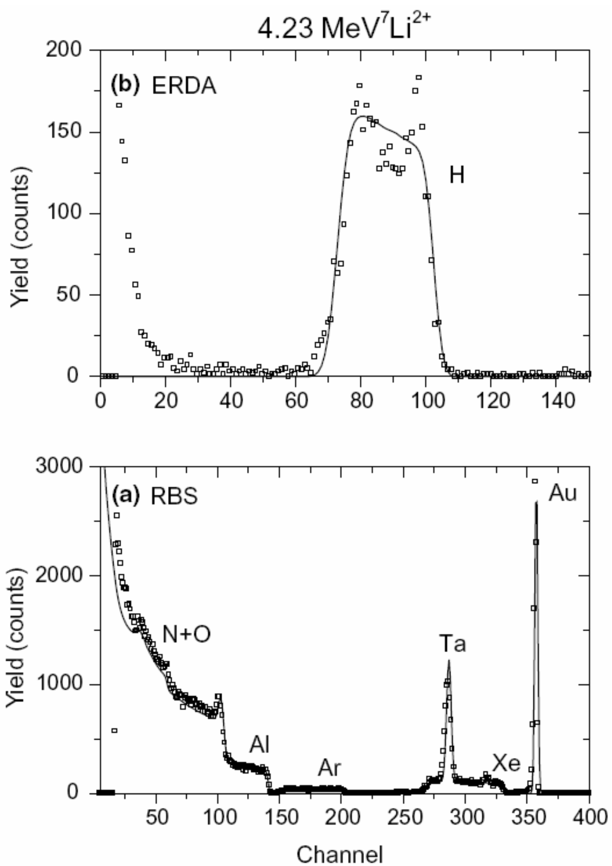
G. Vizkelethy, Nucl. Instr. Meth. B45 (1990) 1

ERD: Elastic Recoil Detection Analysis

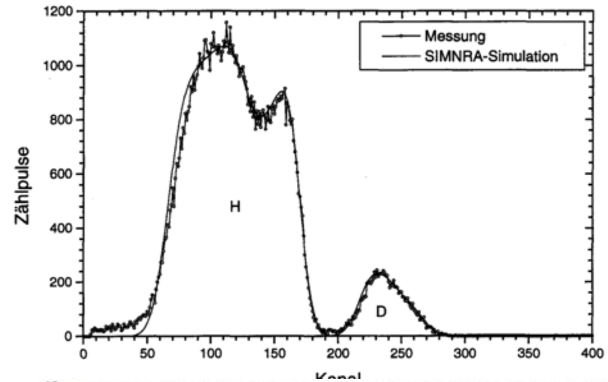
Specific feature:

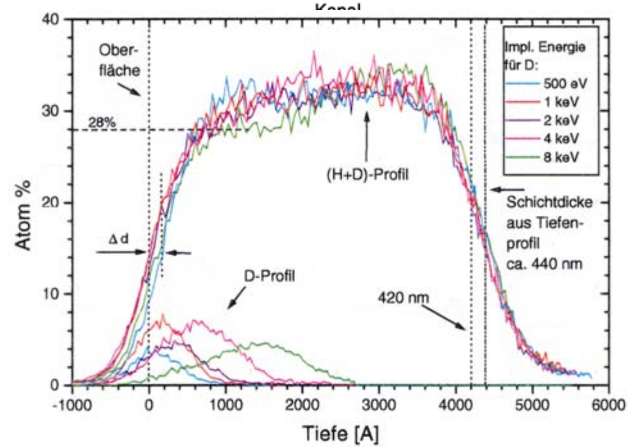
- one of the very few methods to detect hydrogen
- discrimination between hydrogen isotopes possible

2 nm Au / 100 nm AlN / 2 nm Ta / Si



a-C:H layer, implanted with 8 keV D^+
Measurement: 2.6 MeV He, θ=30°





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