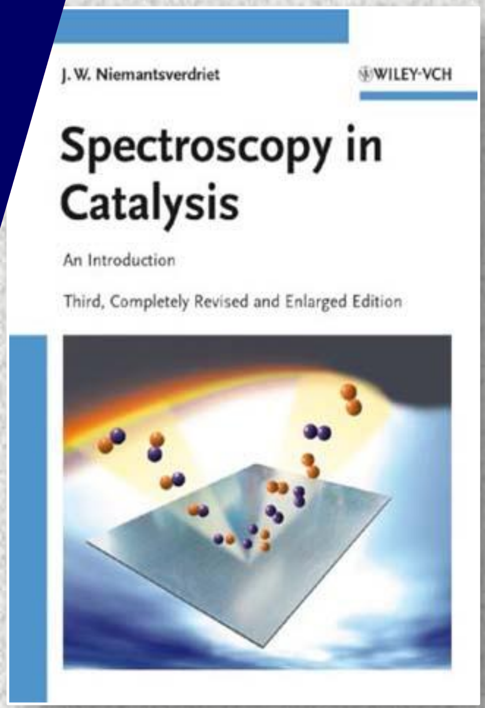
Characterization of solid catalysts

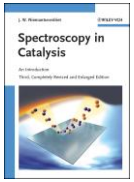
4. Ion Spectroscopy

Prof dr J W (Hans) Niemantsverdriet
Schuit Institute of Catalysis

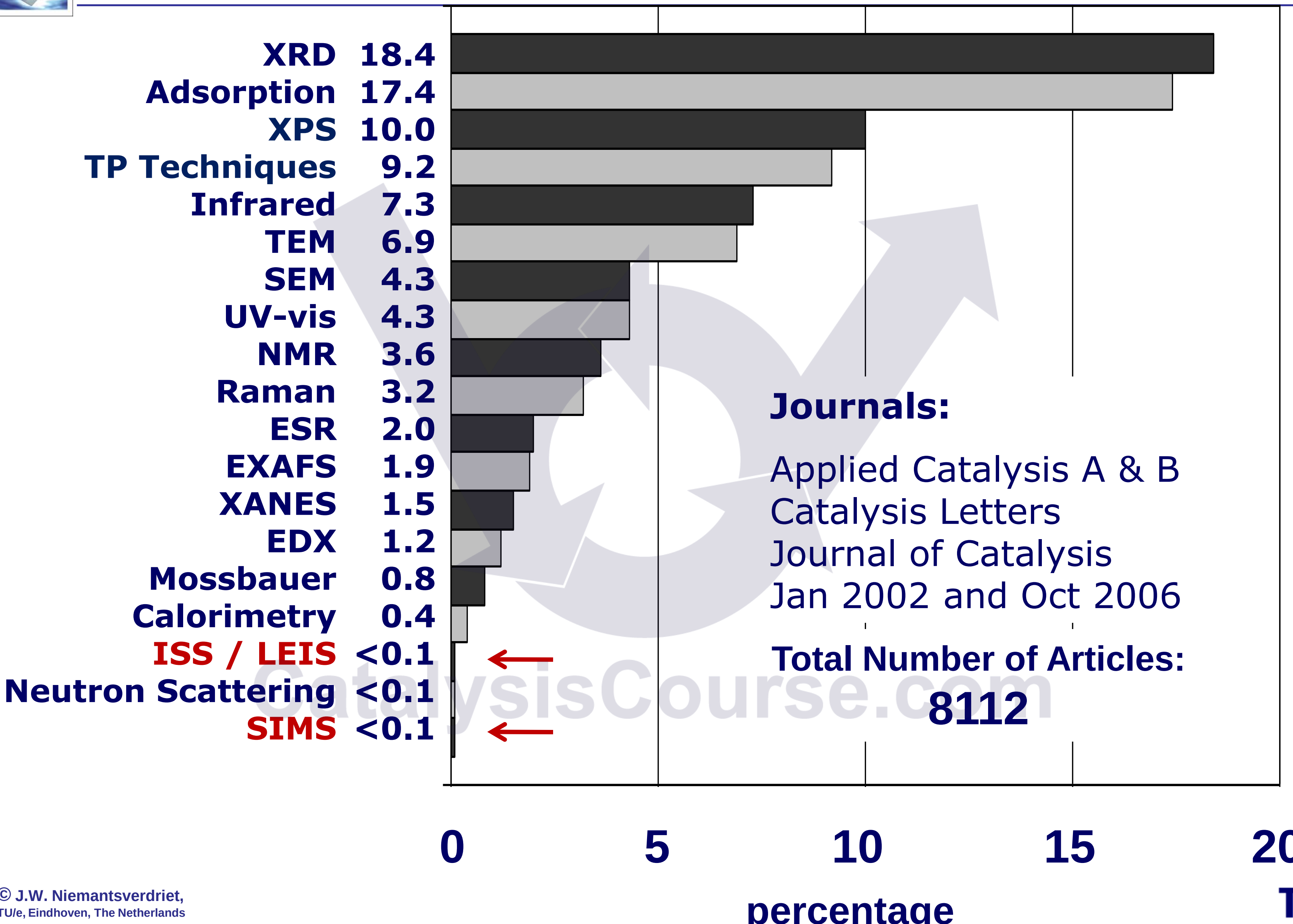


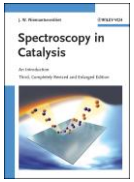
TU/e Technische Universiteit Eindhoven University of Technology

Where innovation starts



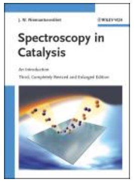
How often are techniques used



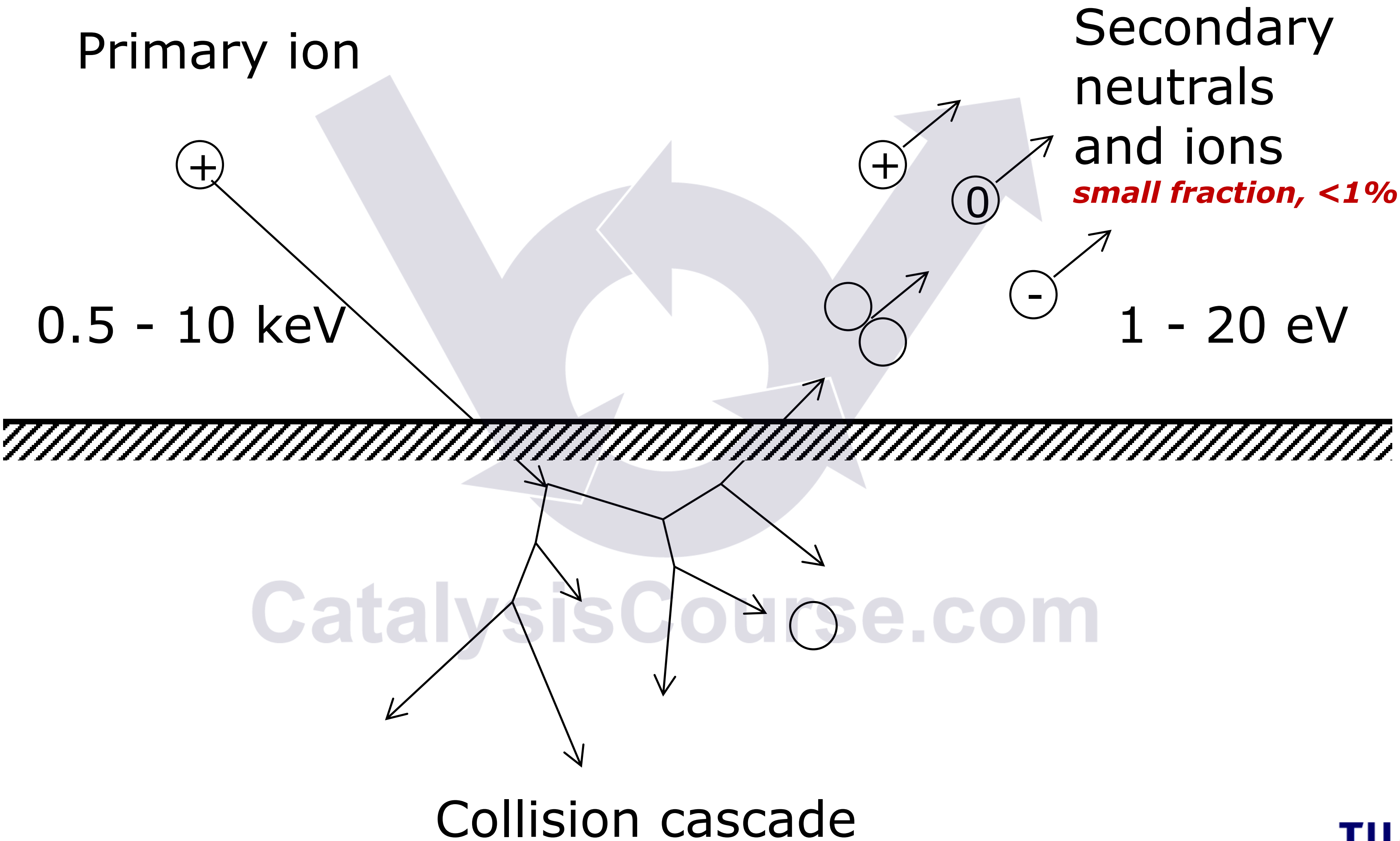


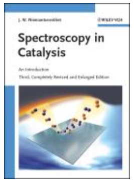
Ion Spectroscopy

SIMS	secondary ion mass spectrometry
SNMS	secondary neutral mass spectrometry
ISS	ion scattering spectroscopy
RBS	Rutherford backscattering spectroscopy
LEIS	low energy ion spectroscopy

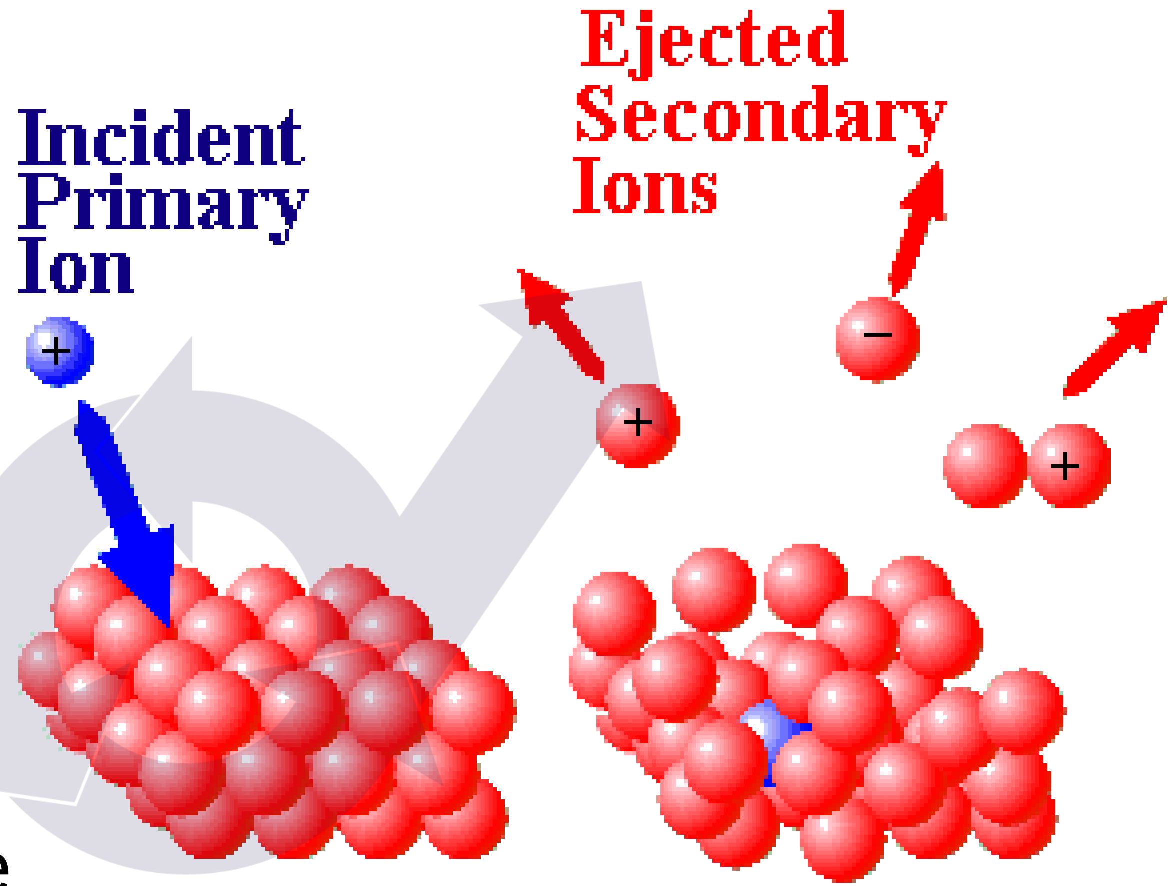


Secondary Ion Mass Spectrometry





Static & Dynamic SIMS



Courtesy VG

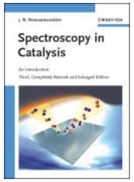
Static = low damage

Monolayer removed in minutes

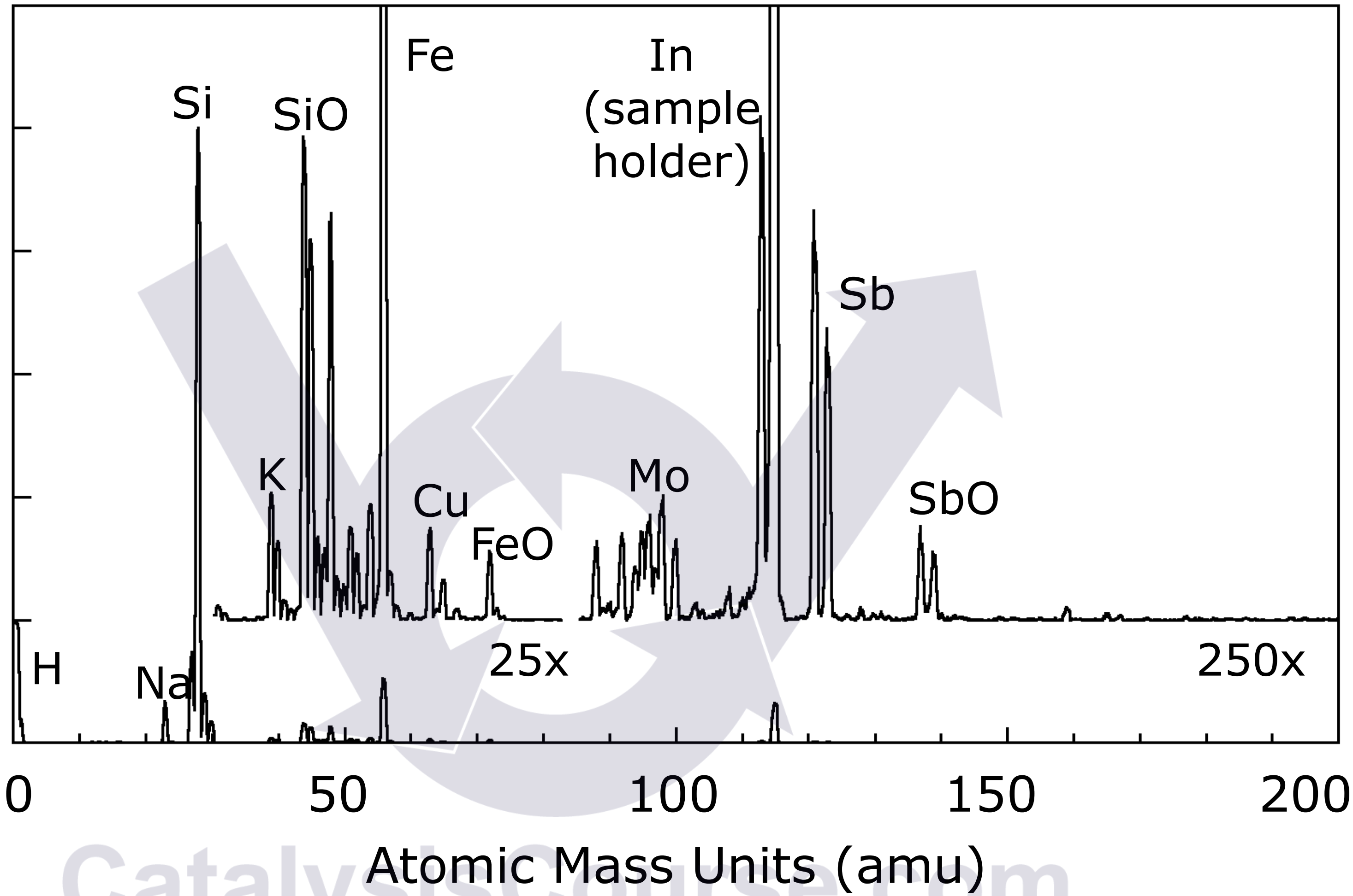
Dynamic = sputtering

Several layers per second removed

TU/e



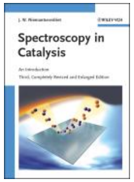
SIMS Fe-Sb-Oxide Ammoxidation Catalyst



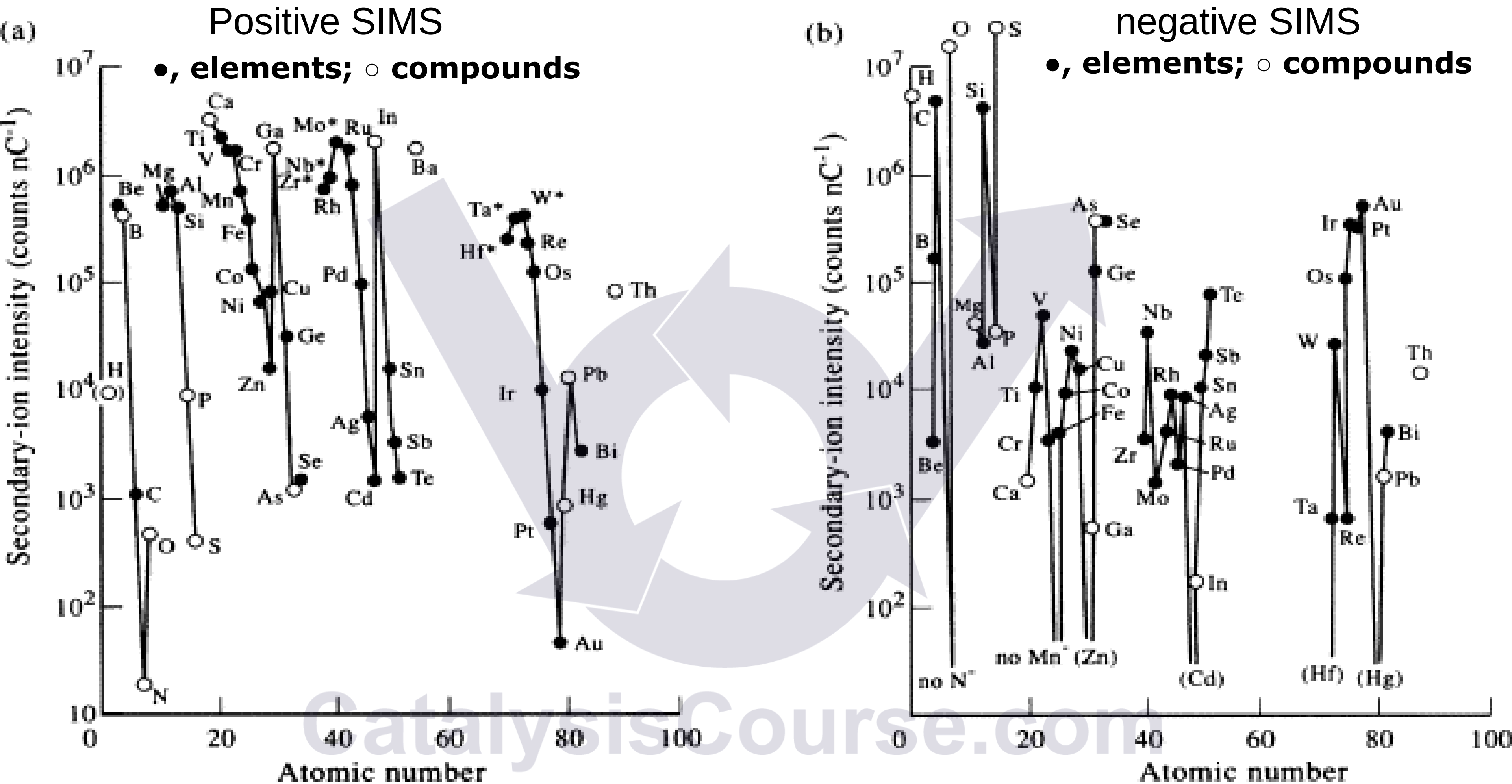
Herman Borg & Pieter Gunter, TU/e 1990

1) **SIMS reveals all elements (also trace amounts)**
2) **Note the important role of isotopes in the identification of species**

TU/e



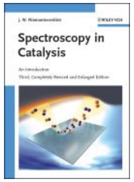
SIMS Intensities vary strongly over the periodic table



H.A. Storms, K.F. Brown and J.D. Stein, *Anal. Chem.* **49** (1977) 2023

SIMS intensities also vary strongly with oxidation state and environment; this makes quantification very difficult

TU/e



SIMS intensity:

$$I_s^{\pm} = I_p \, Y \, R^{\pm} \, c^{surf} \, T$$

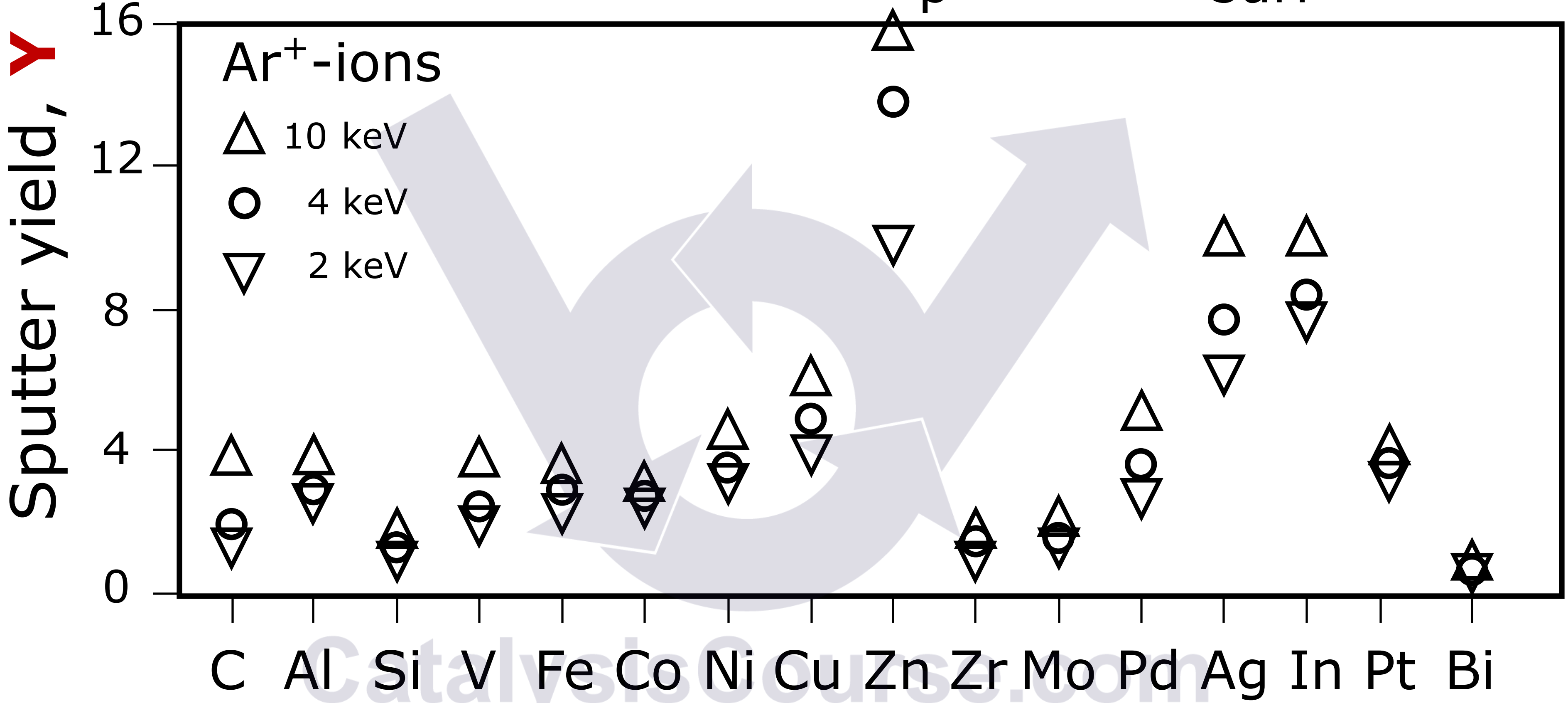
with

I_s	**intensity of secondary ions (=rate in counts per sec)**
I_p	**flux of primary ions**
Y	**sputter yield (number of atoms ejected per incident ion)**
R	**probability that particle leaves as positive or negative ion**
c^{surf}	**fractional concentration of the element in the surface**
T	**transmission of the mass spectrometer,**

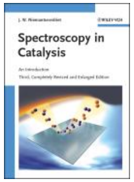
(typically 10^{-3} for quadrupole; 10^{-1} for time-of-flight)

Sputter yields Y are well known

$$\text{Intensity: } I^{\pm} = I_p \, Y \, R^{\pm} \, c_{surf} \, T$$



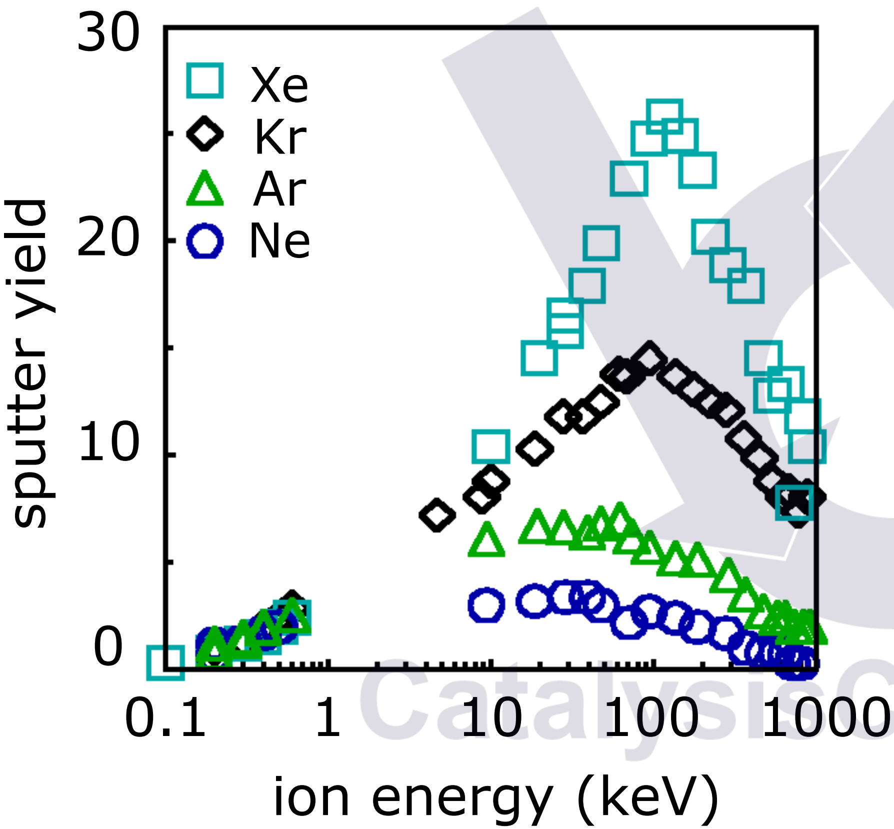
Data from:
J.C. Vickerman, A. Brown, and N.M. Reed (Eds.), Secondary Ion Mass Spectrometry, Principles and Applications, Clarendon, Oxford, 1989.

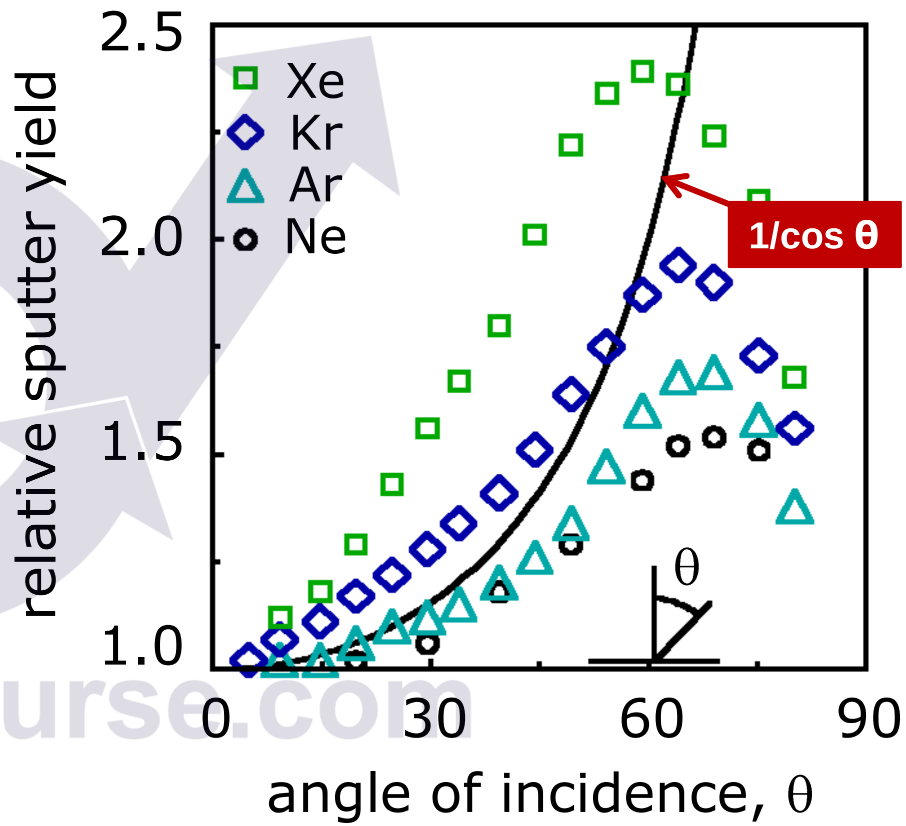


SIMS: Sputter Yields

depend on the primary ion mass and on impact geometry

$$\text{Intensity: } I^{\pm} = I_p \, \mathbf{Y} \, R^{\pm} \, c_{surf} \, T$$





Data from: H. Oechsner, Z. Phys. 261 (1973) 37

ionization probability

in a conceptual, but qualitative model;
depends on probabilities of ionization
and reneutralization upon emission

$$R^+ \propto e^{\,const\,\frac{\varphi - I}{v}}$$

R+ ionization probability

φ work function of the sample

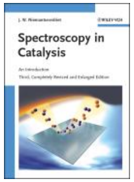
high work function: less chance of neutralization

I ionization potential sputtered particle

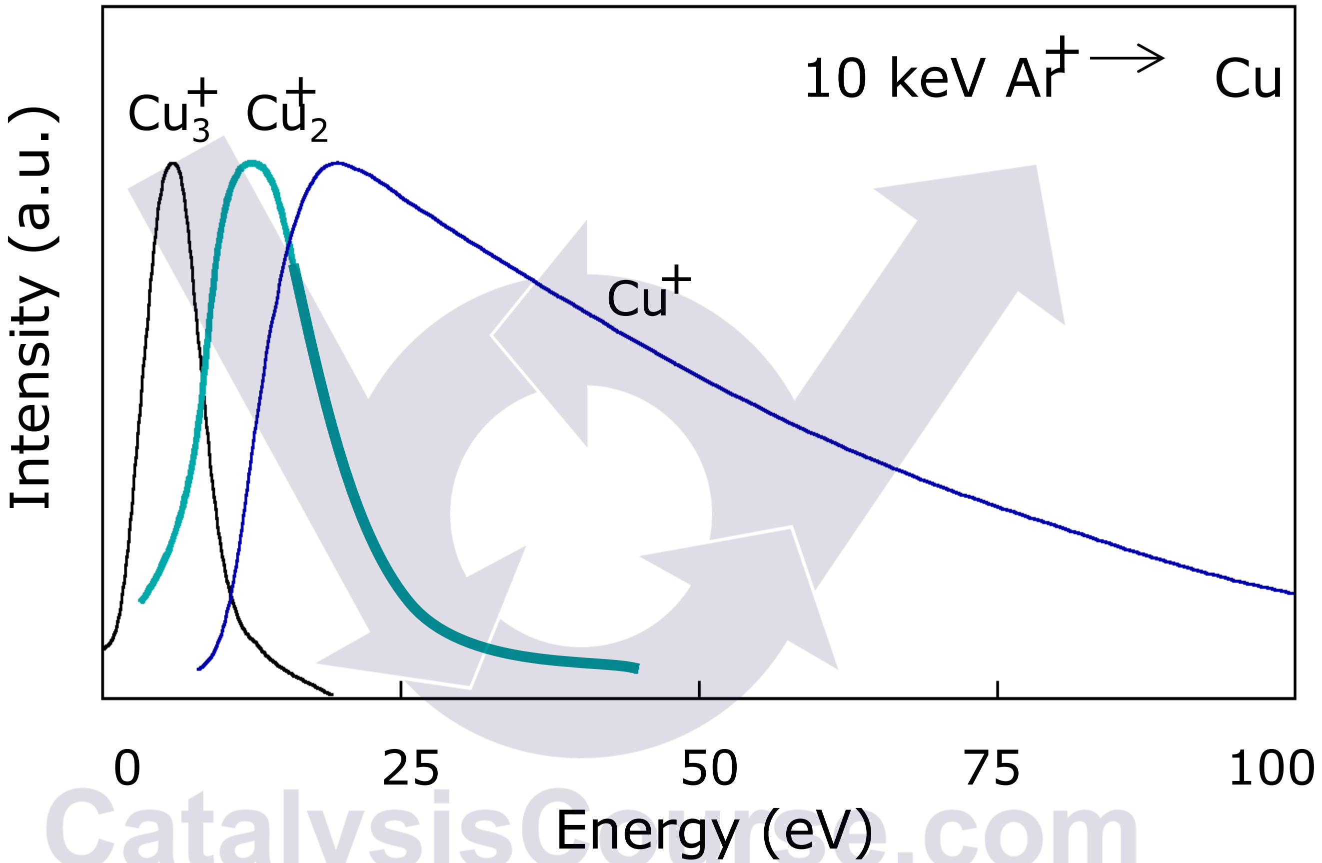
low I: higher probability of ionization

v velocity of the emitted particle

J.K. Norskov and B.I. Lundqvist, Phys. Rev. B 19 (1979) 5661



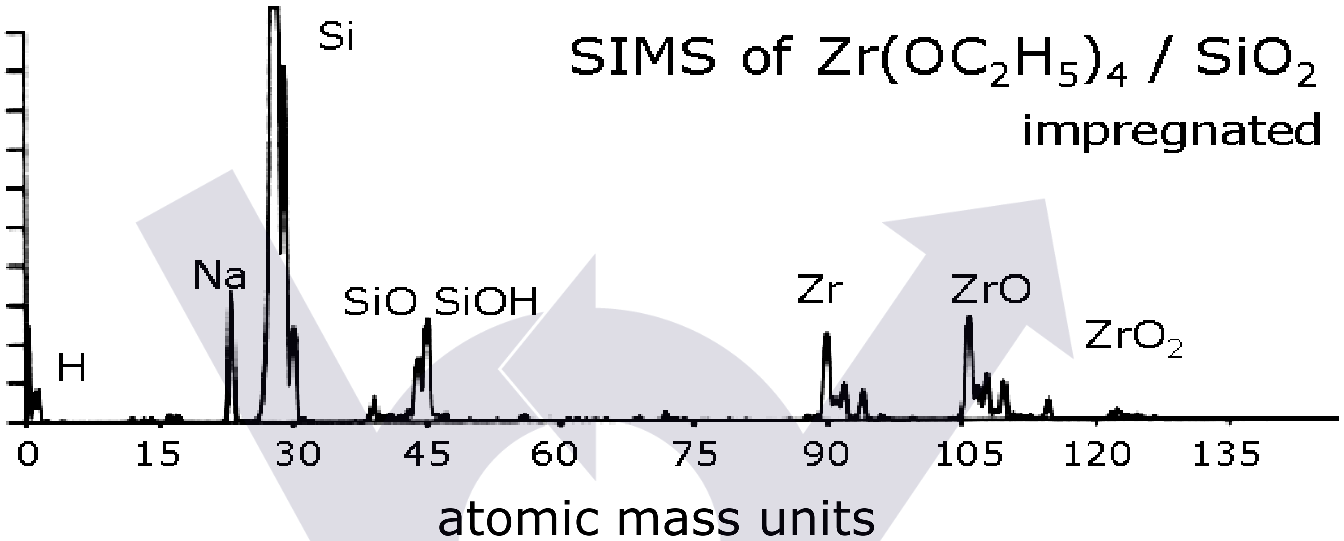
SIMS: Energy Distribution of Secondaries



Implications for charging!

TU/e

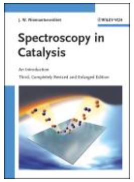
SIMS: Information in Relative Intensities



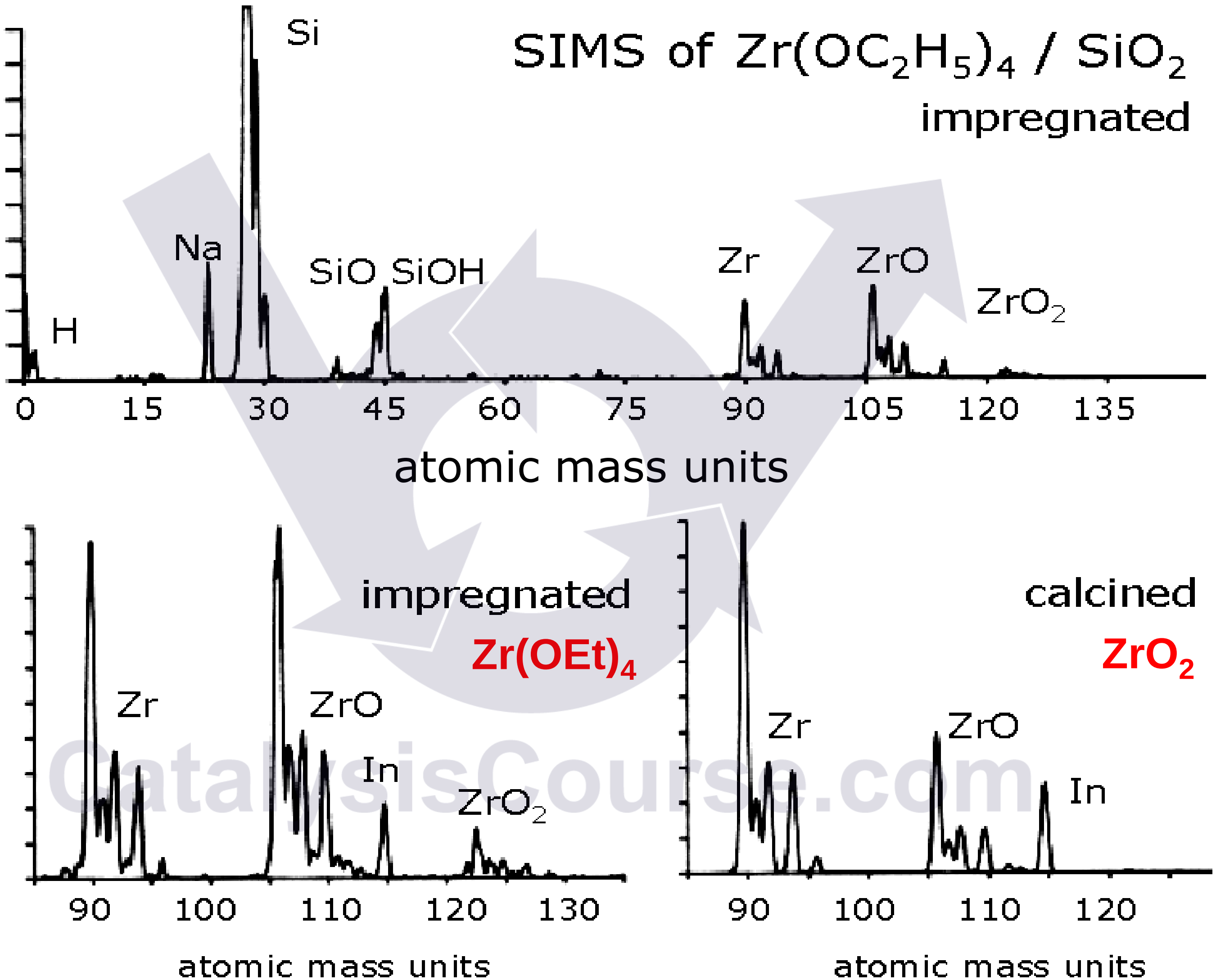
Relative Intensities Zr – ZrO – ZrO2

reflect coordination around Zr:

A.C.Q.M. Meijers, A.M. de Jong, L.M.P. van Gruijthuijsen, J.W. Niemantsverdriet, Appl. Catal. 70 (1991) 53



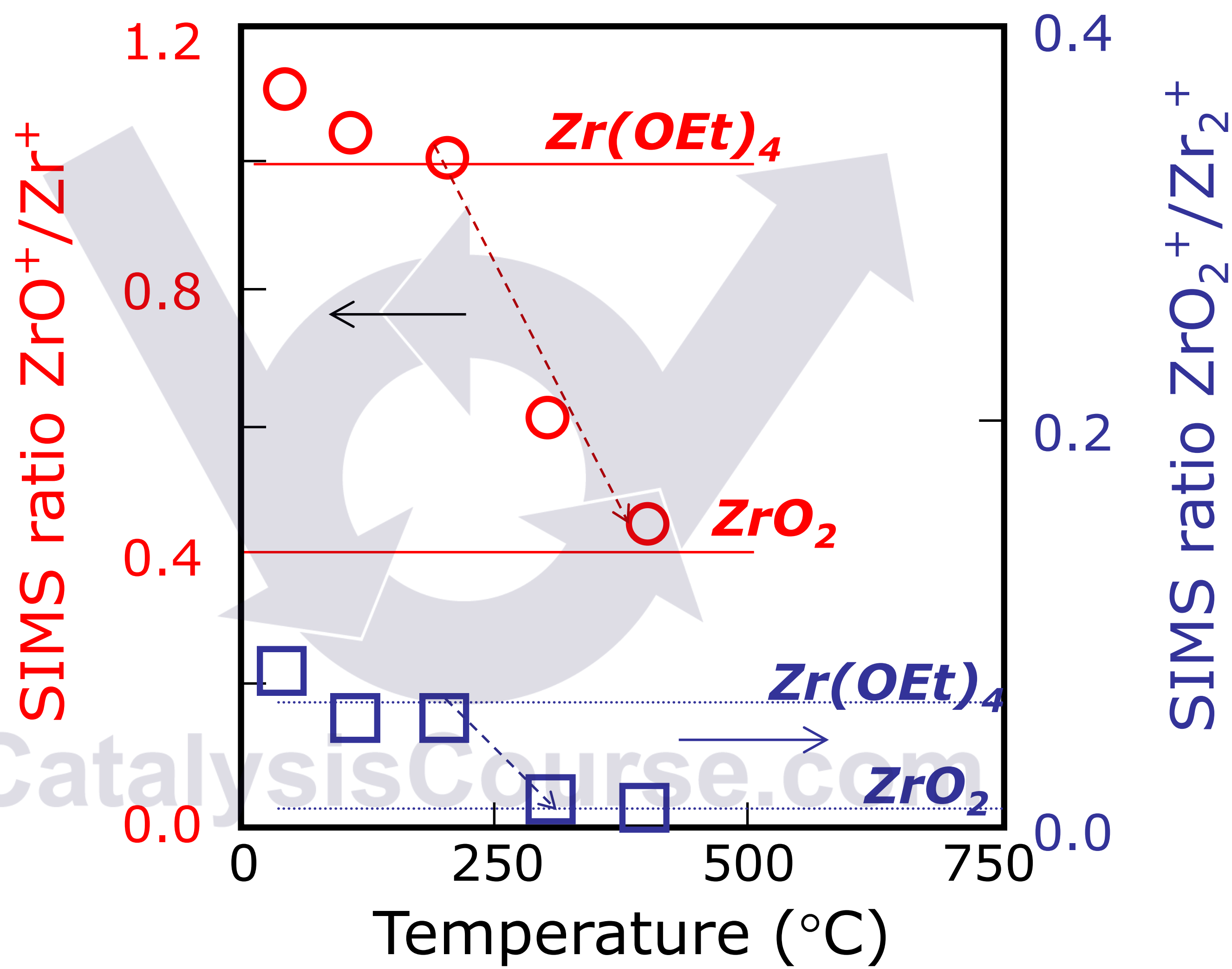
SIMS: Information in Relative Intensities



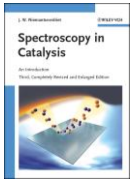
A.C.Q.M. Meijers, A.M. de Jong, L.M.P. van Gruijthuijsen, J.W. Niemantsverdriet, Appl. Catal. 70 (1991) 53

SIMS Reveals Conversion $Zr(OEt)_4$ to ZrO_2

versus calcination temperature

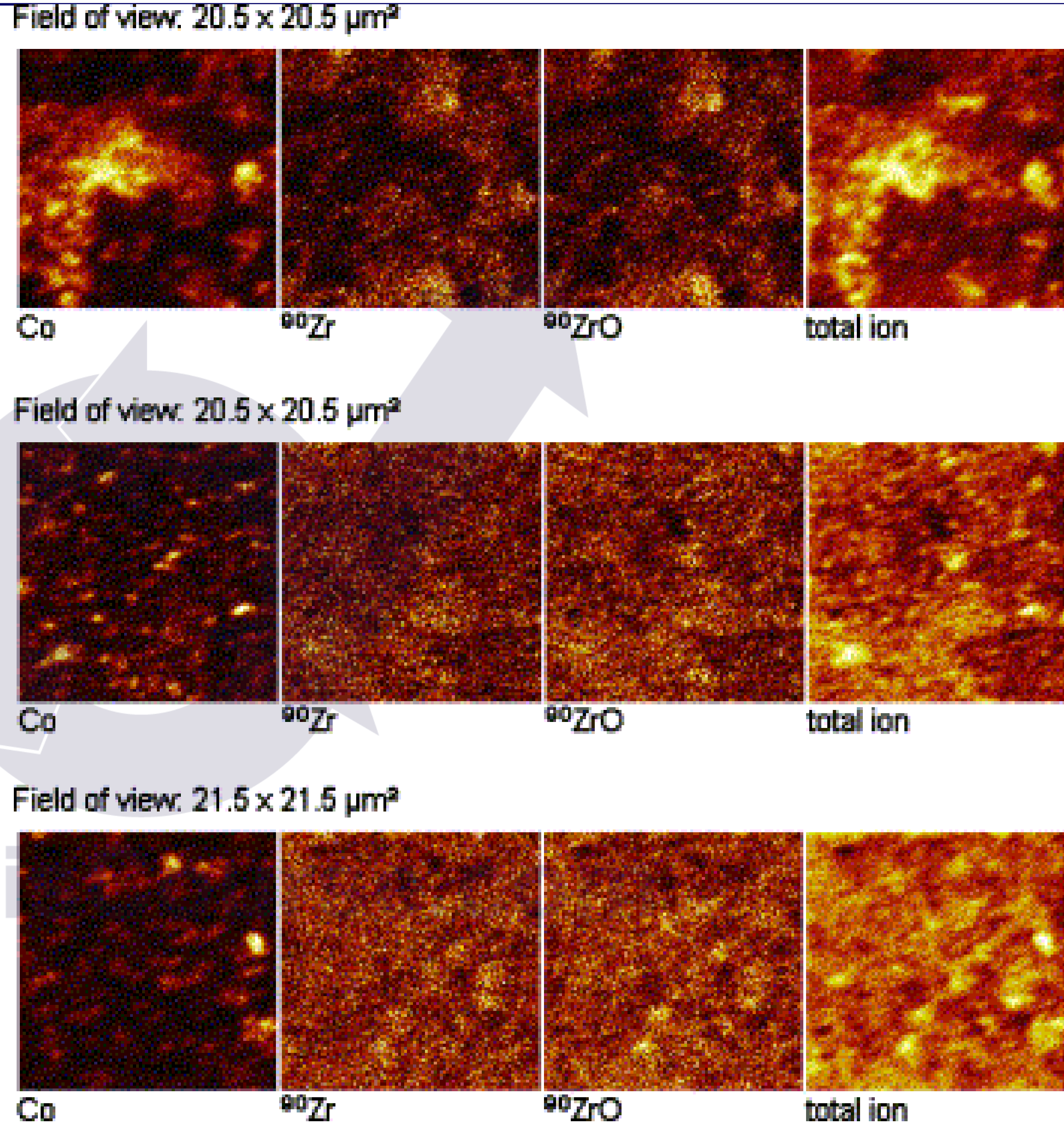


A.C.Q.M. Meijers, A.M. de Jong, L.M.P. van Gruijthuijsen, J.W. Niemantsverdriet, Appl. Catal. 70 (1991) 53



Imaging by SIMS: Chemical Maps

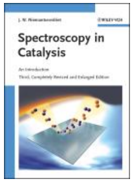
TOF-SIMS Co/ZrO2 Catalysts



TOF-SIMS high resolution images of 9.9%Co/ZrO2 catalyst calcined at 350 °C for 3 h. Bright colour indicates investigated ions. Images collected from different surface areas.

J. Grams, J. Góralski and T. Paryjczak, Surface Sci. 549 (2004) L21

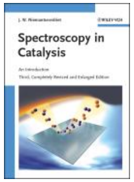
TU/e



Ion Spectroscopy

SIMS	secondary ion mass spectrometry
SNMS	secondary neutral mass spectrometry
ISS	ion scattering spectroscopy
RBS	Rutherford backscattering spectroscopy
LEIS	low energy ion spectroscopy

TU/e



SNMS intensity:

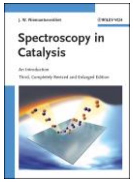
$$I_s^{\pm} = I_p \, Y \, \cancel{R^{\pm}} \, c^{surf} \, T$$

$R^{\pm} \approx 1$

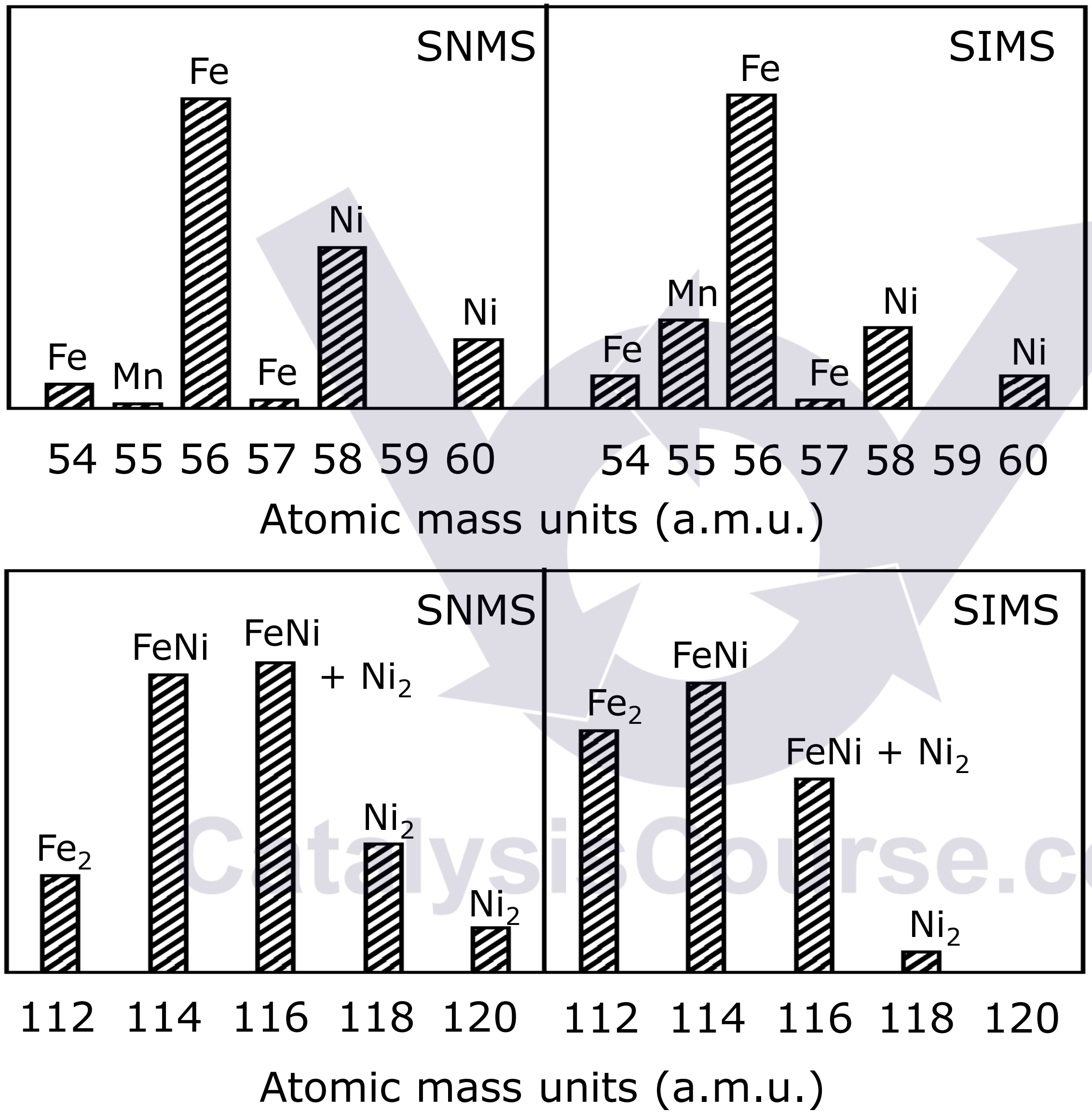
with

I_s	**intensity of secondary ions (=rate in counts per sec)**
I_p	**flux of primary ions**
Y	**sputter yield (number of atoms ejected per incident ion)**
c^{surf}	**fractional concentration of the element in the surface**
T	**ionization efficiency of the mass spectrometer (low!!)**

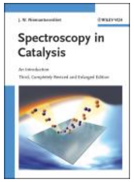
TU/e



SIMS & SNMS 1:1 Fe-Ni Alloy



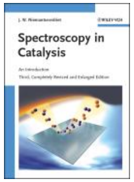
SNMS better quantifiable,
but relatively insensitive



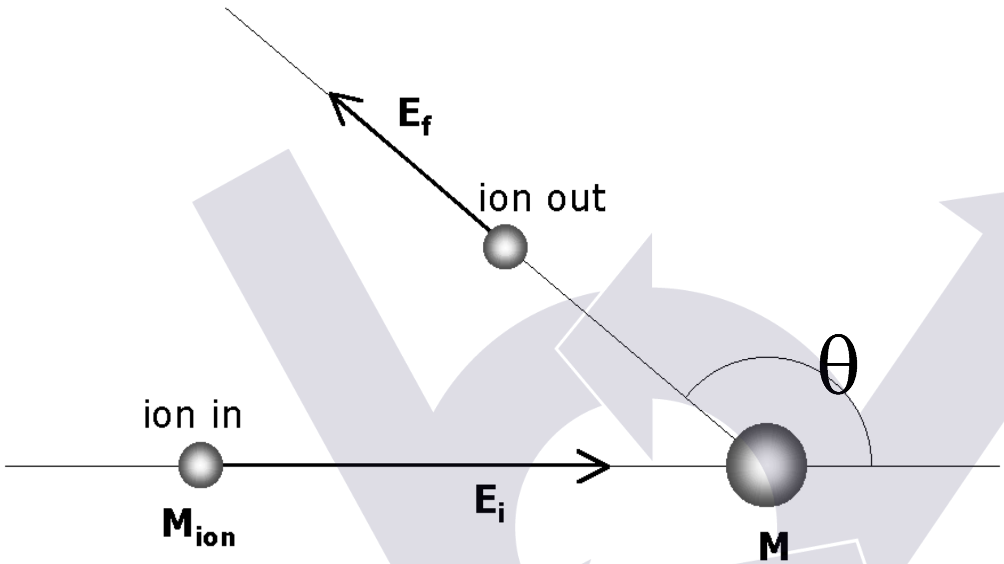
Ion Spectroscopy: SIMS

SIMS:

- detection of trace amounts
- molecular information via clusters
- quantification difficult



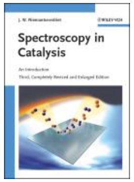
Ion Scattering Spectroscopy



$$K_M = \frac{E_f}{E_i} = \left(\frac{(M^2 - M_{ion}^2 \sin^2\theta)^{1/2} + M_{ion}\cos\theta}{M + M_{ion}} \right)^2$$

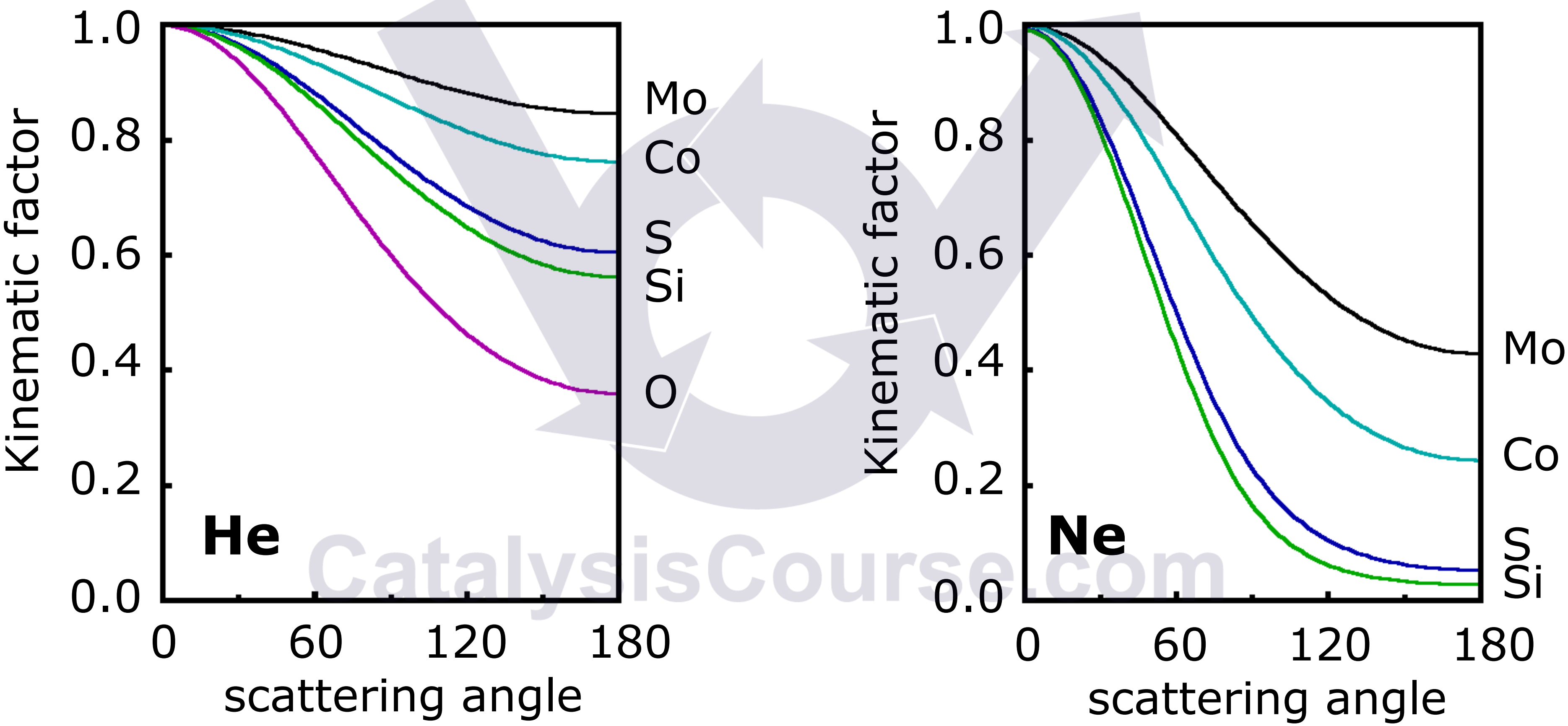
$$E_f = \textit{Mass Spectrum !!}$$

TU/e

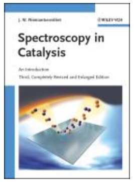


Ion Scattering & Energy Resolution

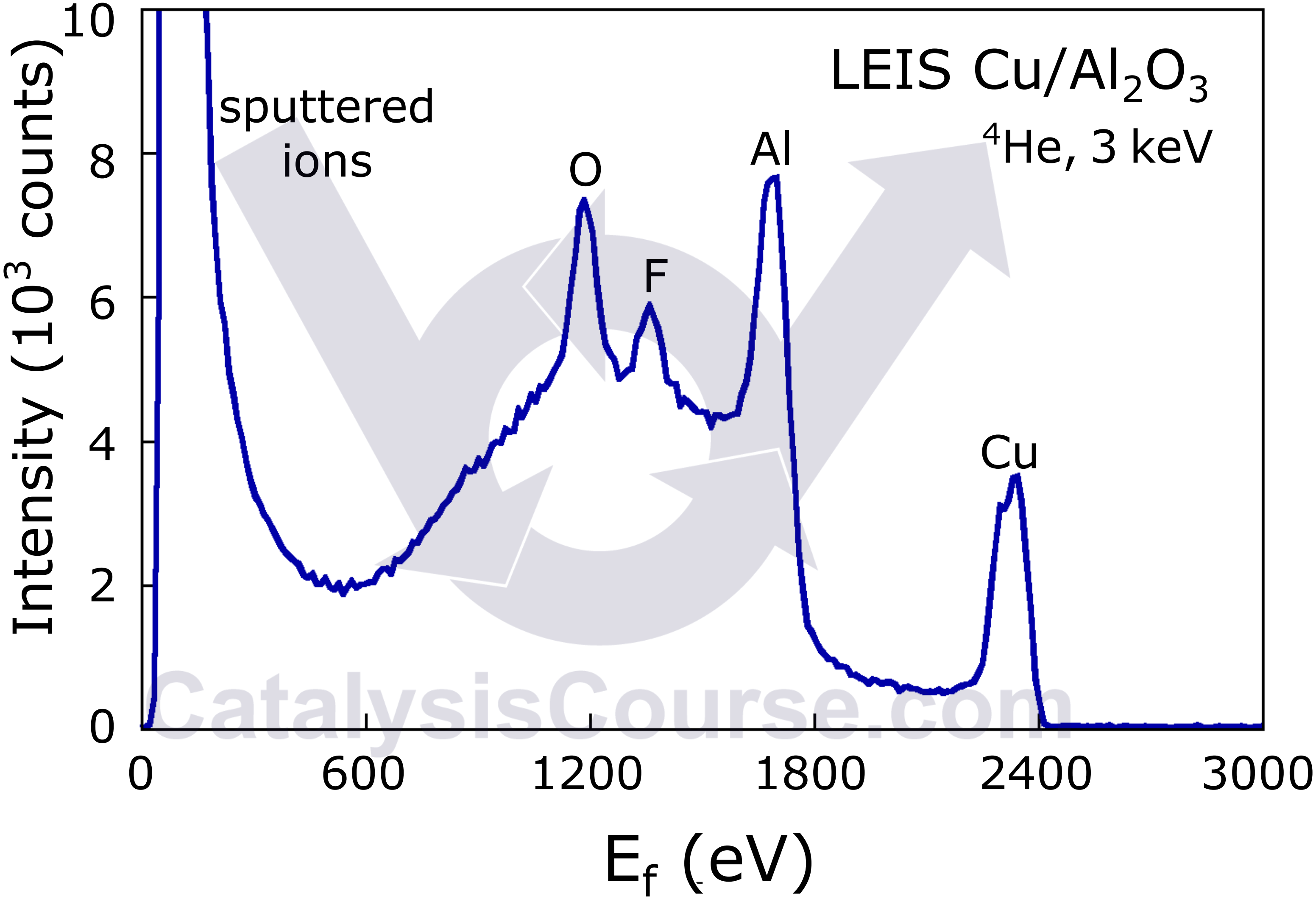
$$K_M = \frac{E_f}{E_i} = \left(\frac{\left(M^2 - M_{ion}^2 \sin^2\theta \right)^{1/2} + M_{ion}\cos\theta}{M + M_{ion}} \right)^2$$



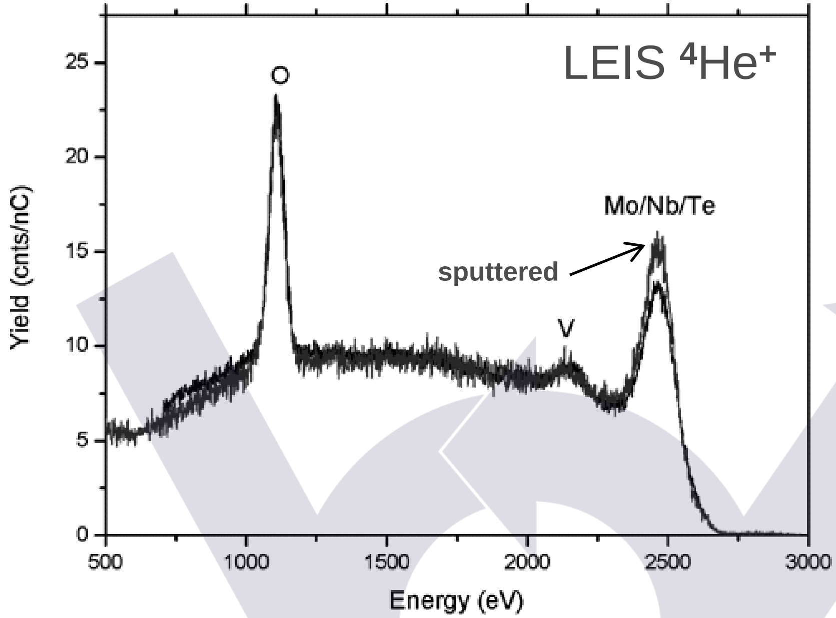
TU/e



Low Energy Ion Scattering



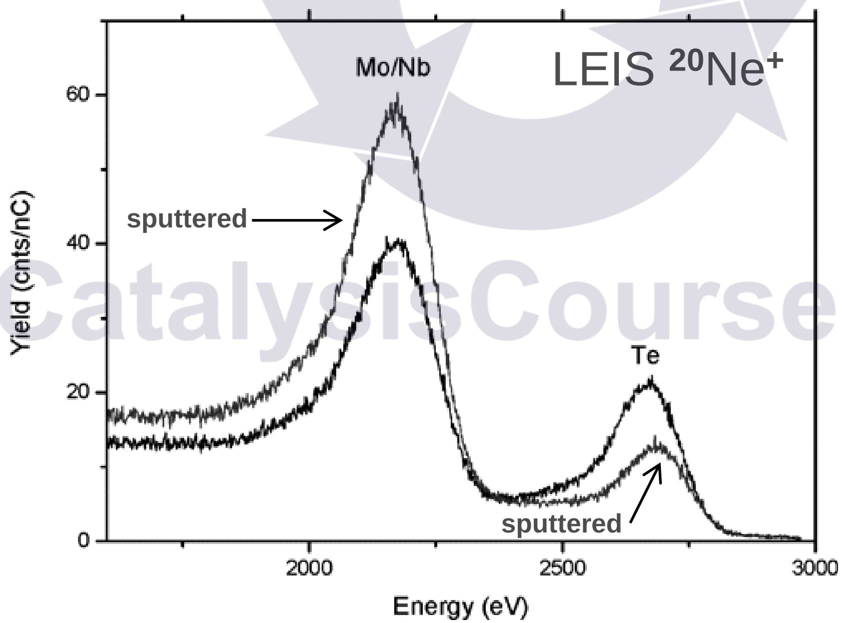
LEIS of V-Mo-Nb-Te mixed metal oxide catalyst



Z		M
8	O	16.00
23	V	50.94
41	Nb	92.90
42	Mo	95.94
52	Te	127.60

Ne scattering:

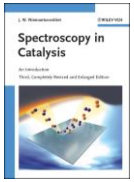
Better resolution for higher mass



Light sputtering preferentially removes Tellurium

V.V. Guliants, R. Bhandari, A.R. Hughett, S. Bhatt, B.D. Schuler, H.H. Brongersma, A. Knoester, A.M. Gaffney, and S. Han, J. Phys. Chem. B 110 (2006) 6129

TU/e



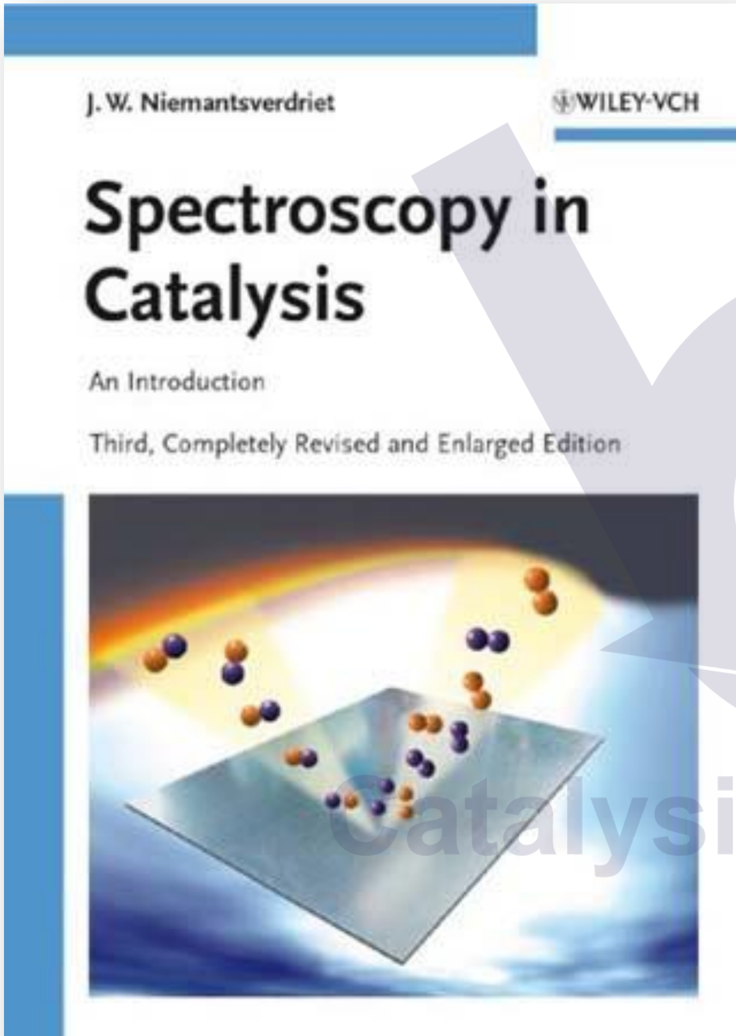
Ion Spectroscopy

SIMS:
- detection of trace amounts
- molecular information via clusters
- quantitation difficult

LEIS
- extreme surface sensitivity
- reasonably quantitative

Download the handout for this lecture from

www.catalysiscourse.com



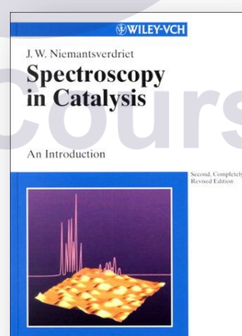
Read more about the ion spectroscopies

in Chapter 4 of

Spectroscopy in Catalysis: An Introduction, Third Edition

J. W. Niemantsverdriet

Copyright *2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim*
ISBN: 978-3-527-31651-9



Version 2000

gives many examples and references to the literature

Technische Universiteit Eindhoven University of Technology