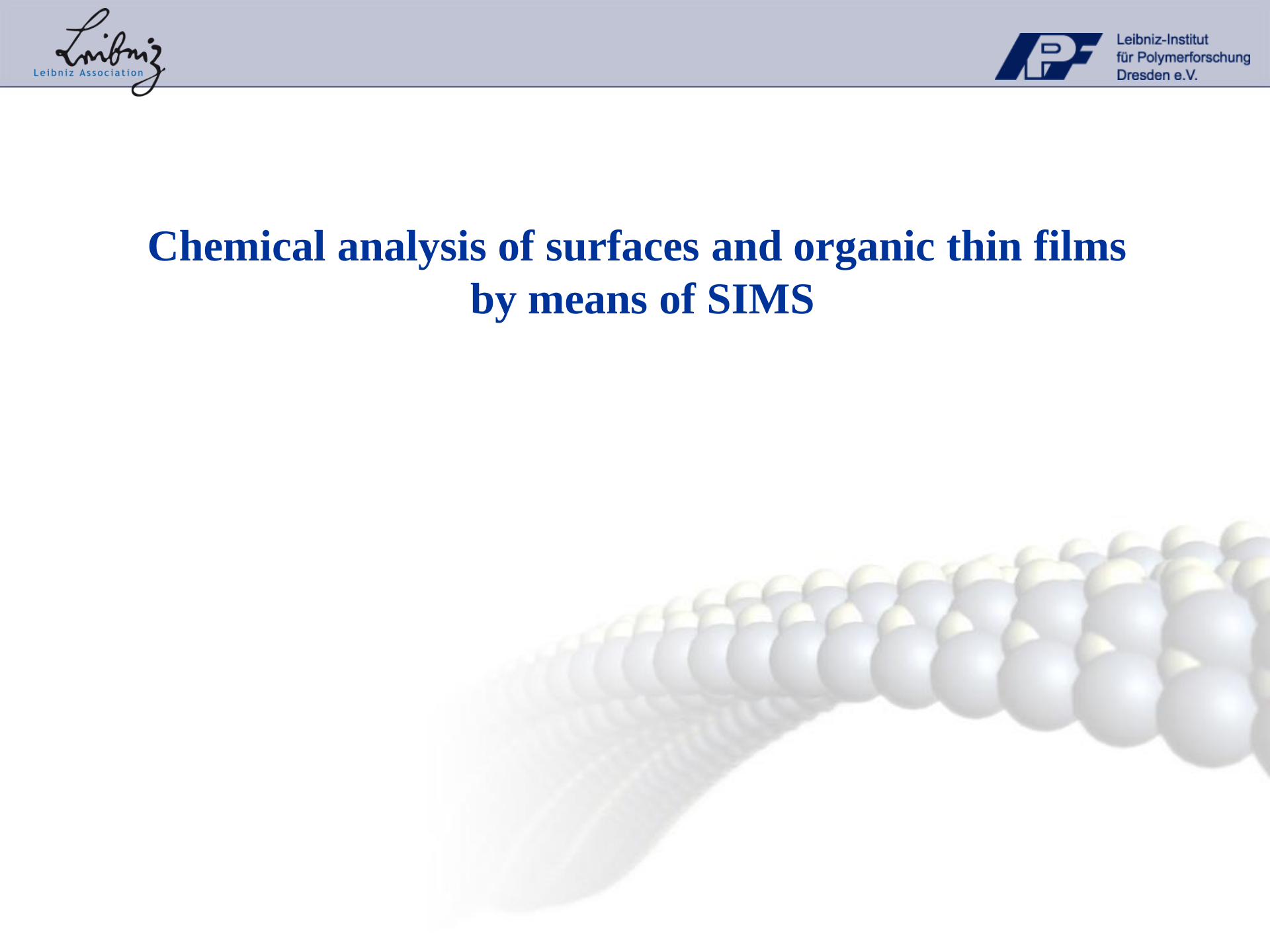
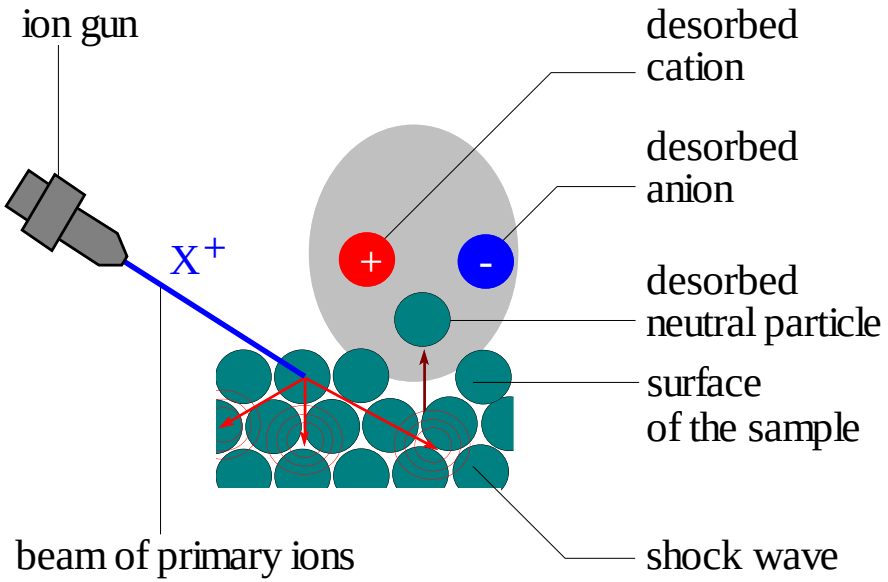
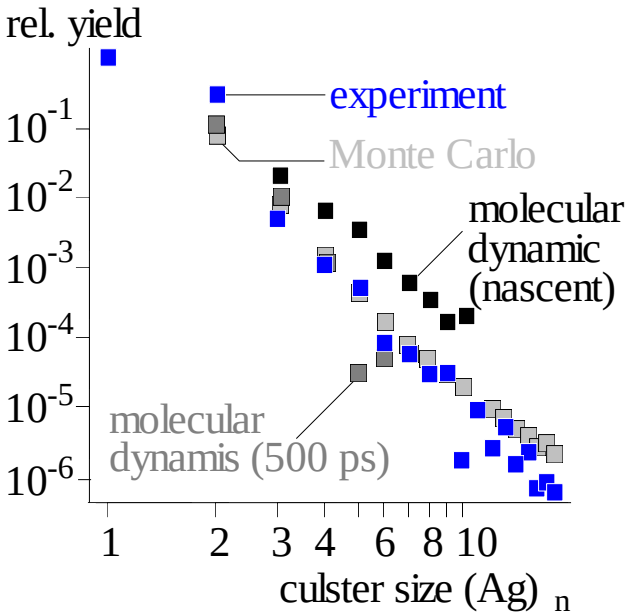
# Chemical analysis of surfaces and organic thin films by means of SIMS

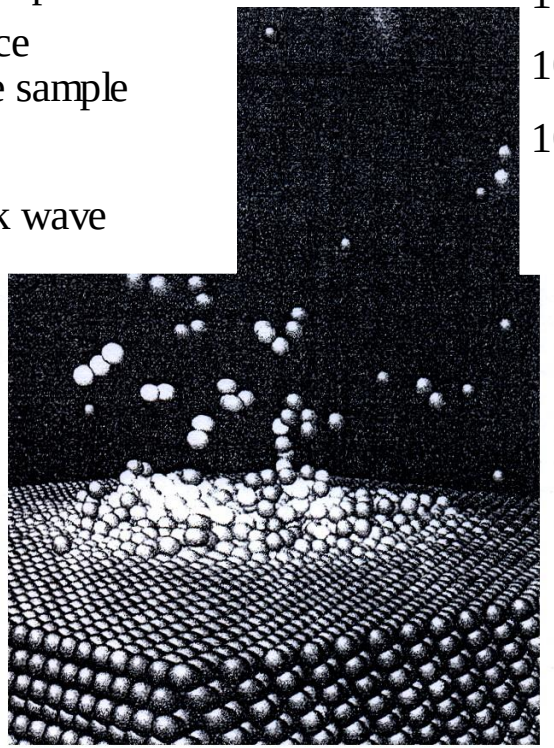


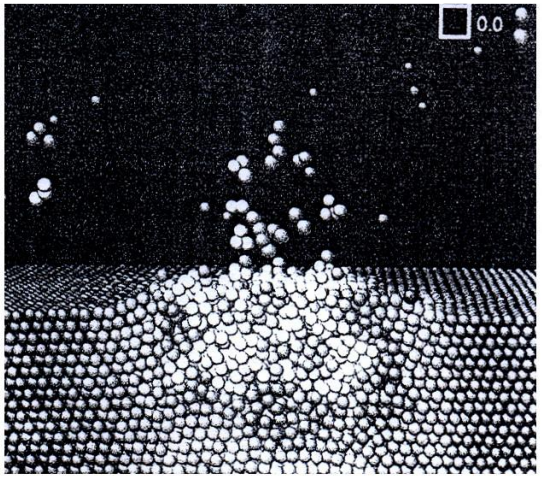
# Secondary ion mass spectrometry (SIMS)

## – Static SIMS (SSIMS) vs. dynamic SIMS –



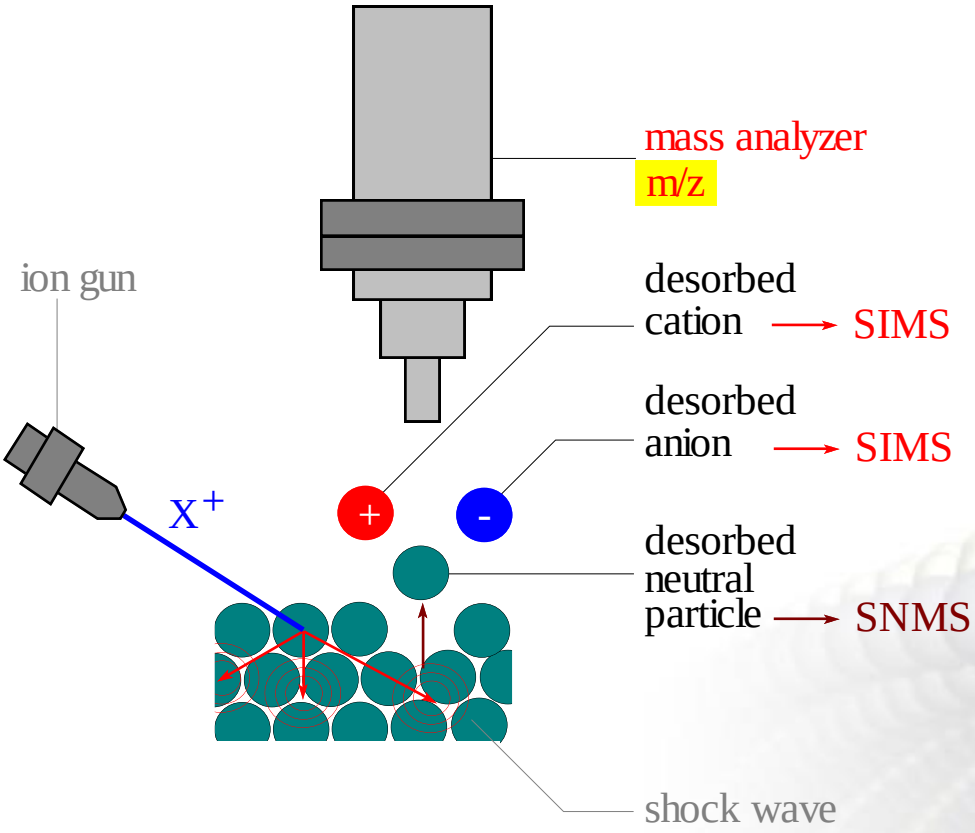



Cu (111) surface 1 ps after the bombardment with a Cu atom having an energy of 5 keV.

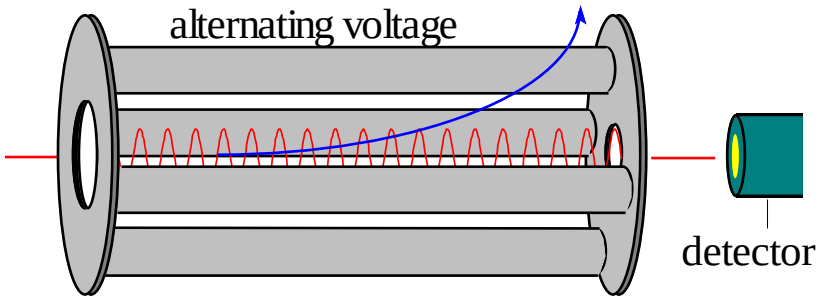
(H.M. Urbassek: Molecular-dynamic simulation of sputtering. Nuclear Instruments and methods in Physics Research, VOL B 122 (1997), S. 427-441)

# Secondary ion mass spectrometry (SIMS)

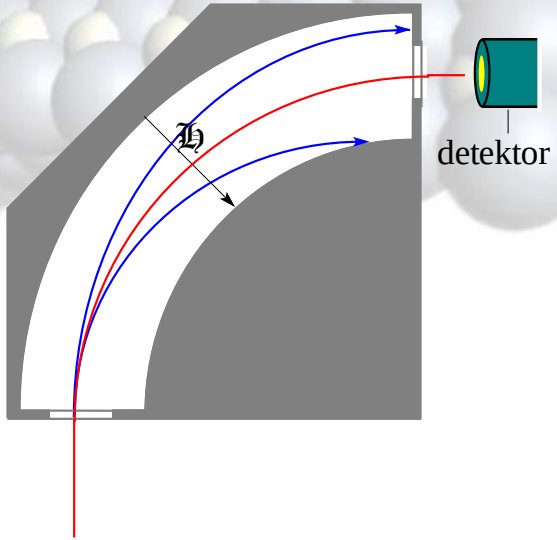
## – Units to separate (molecule) ions of different masses –




Quadruple secondary ion mass spectrometer

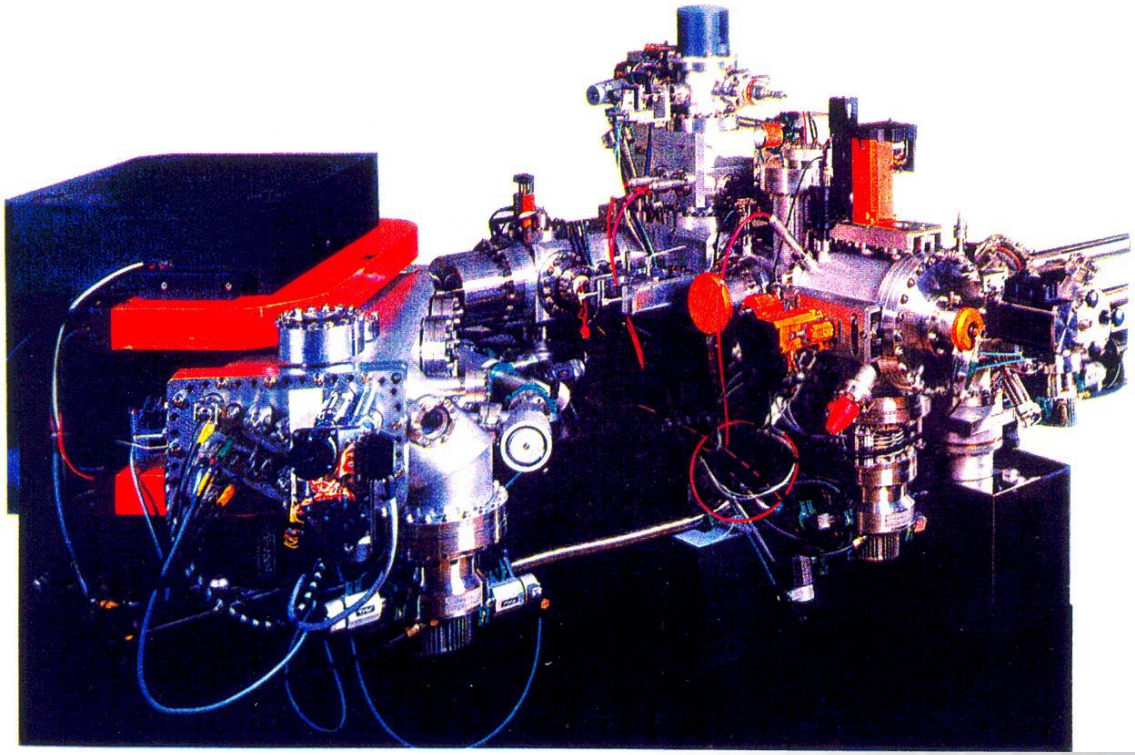


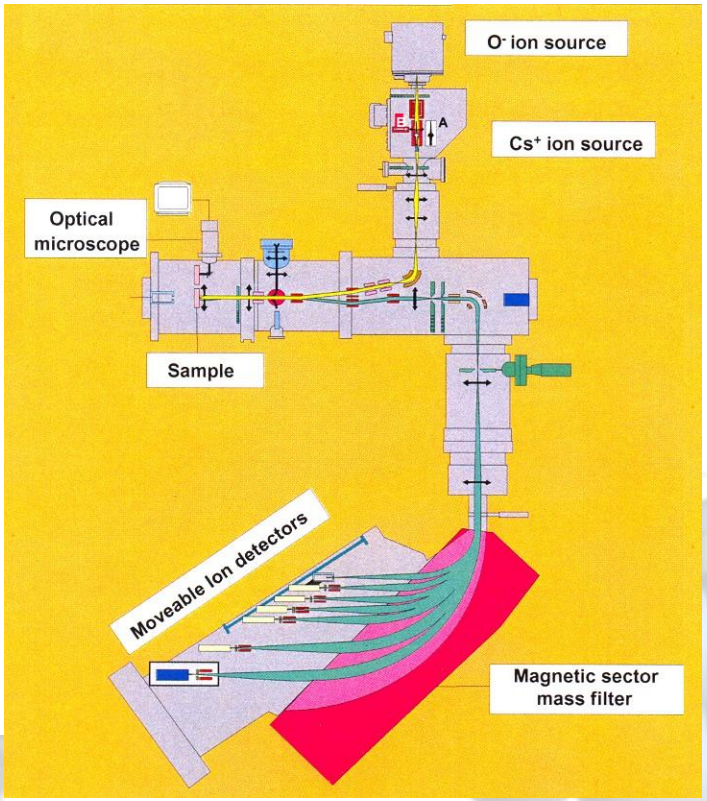

Sector field secondary ion mass spectrometer

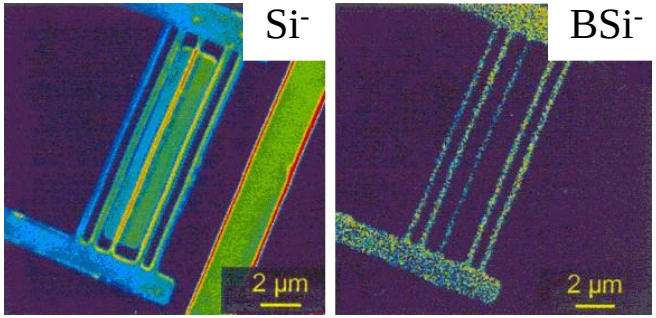


# Sector field secondary ion mass spectrometer

## – NanoSIMS 50 (Cameca, Paris, France) –



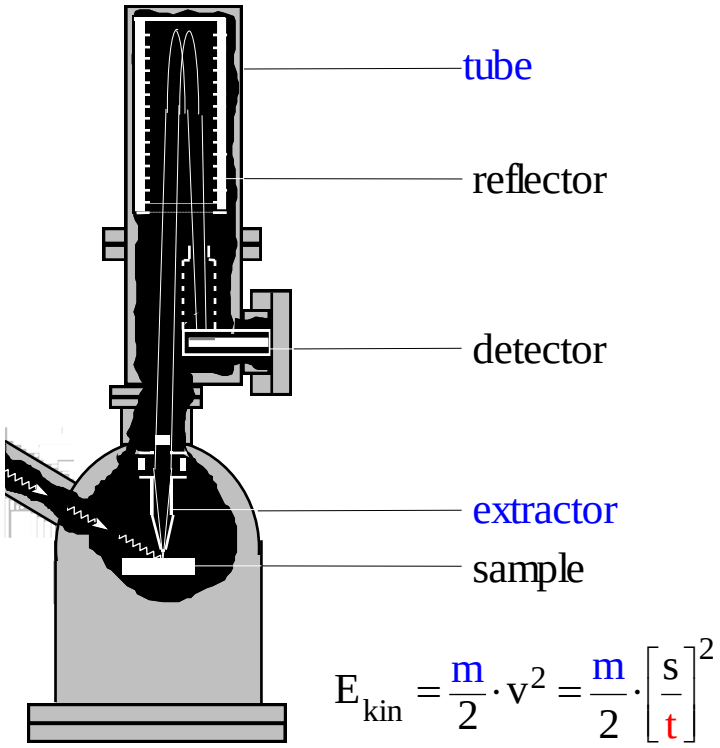


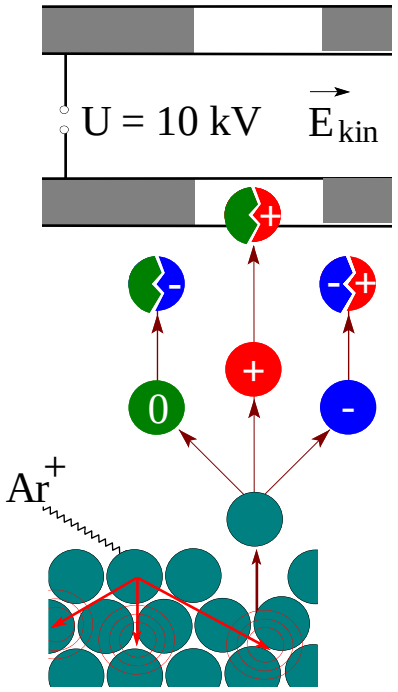

silicon doped with boron,
line width 0,14 µm,
acquisition time: 16 min (ONERA, France)

# Static secondary ion mass spectrometry (SSIMS)

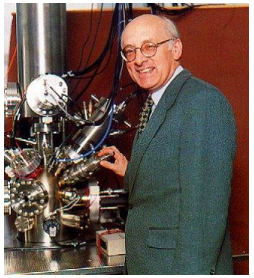
## – Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) –




$$E_{kin} = \frac{m}{2} \cdot v^2 = \frac{m}{2} \cdot \left[\frac{s}{t}\right]^2$$




A. Benninghoven

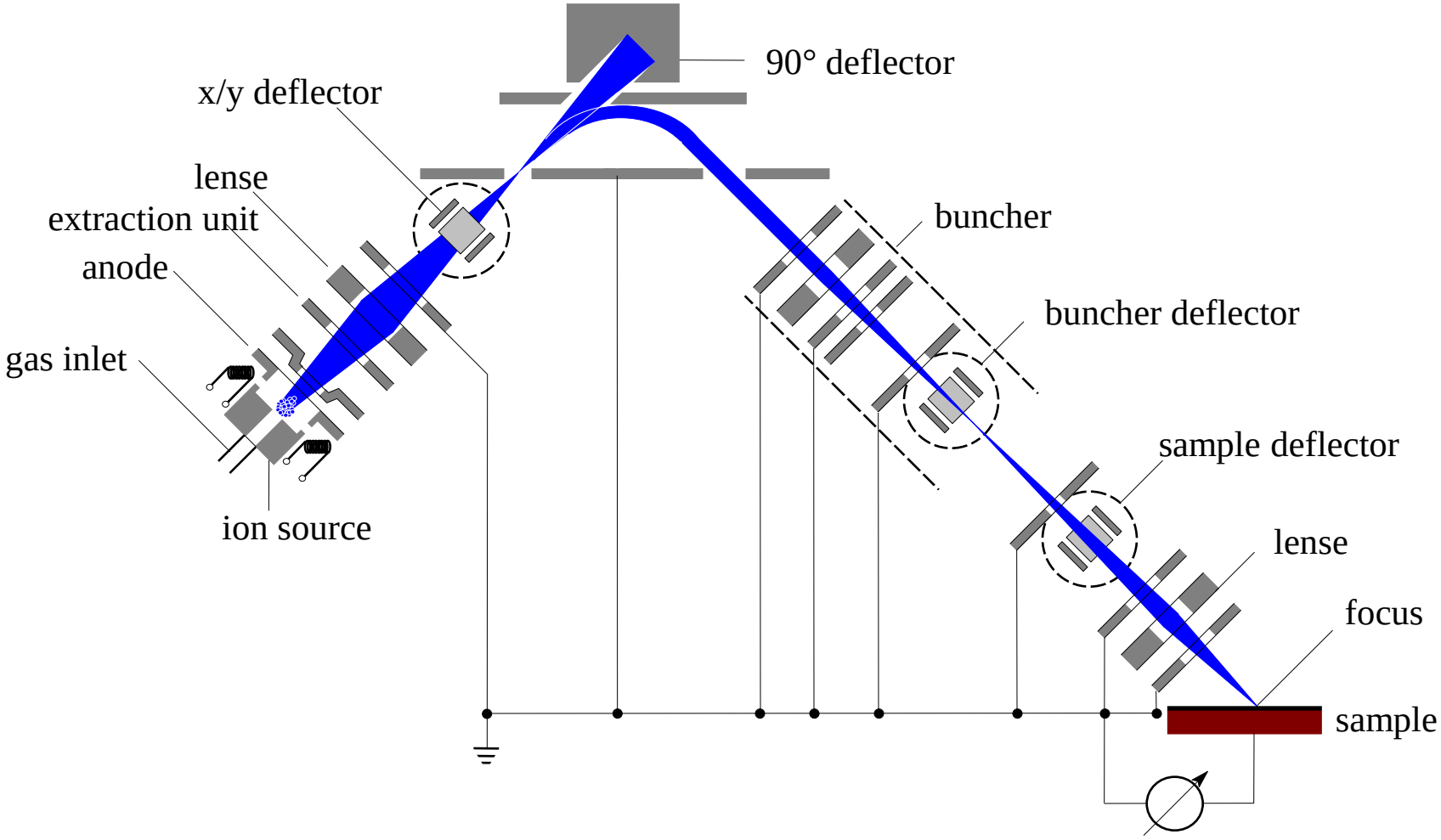


J.C. Vickerman

Charles Evans

# Time-of-Flight Seconday Ion Mass Spectrometry (ToF-SIMS)

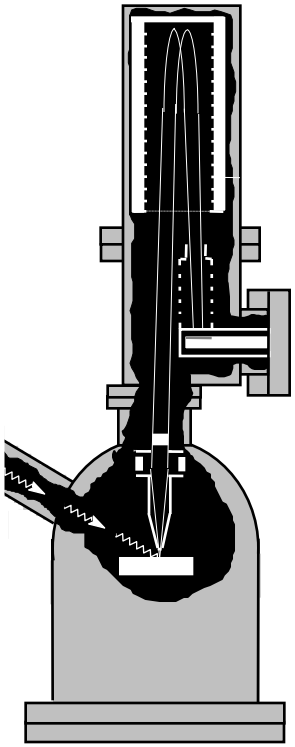
## – Pulsed primary ion beam –



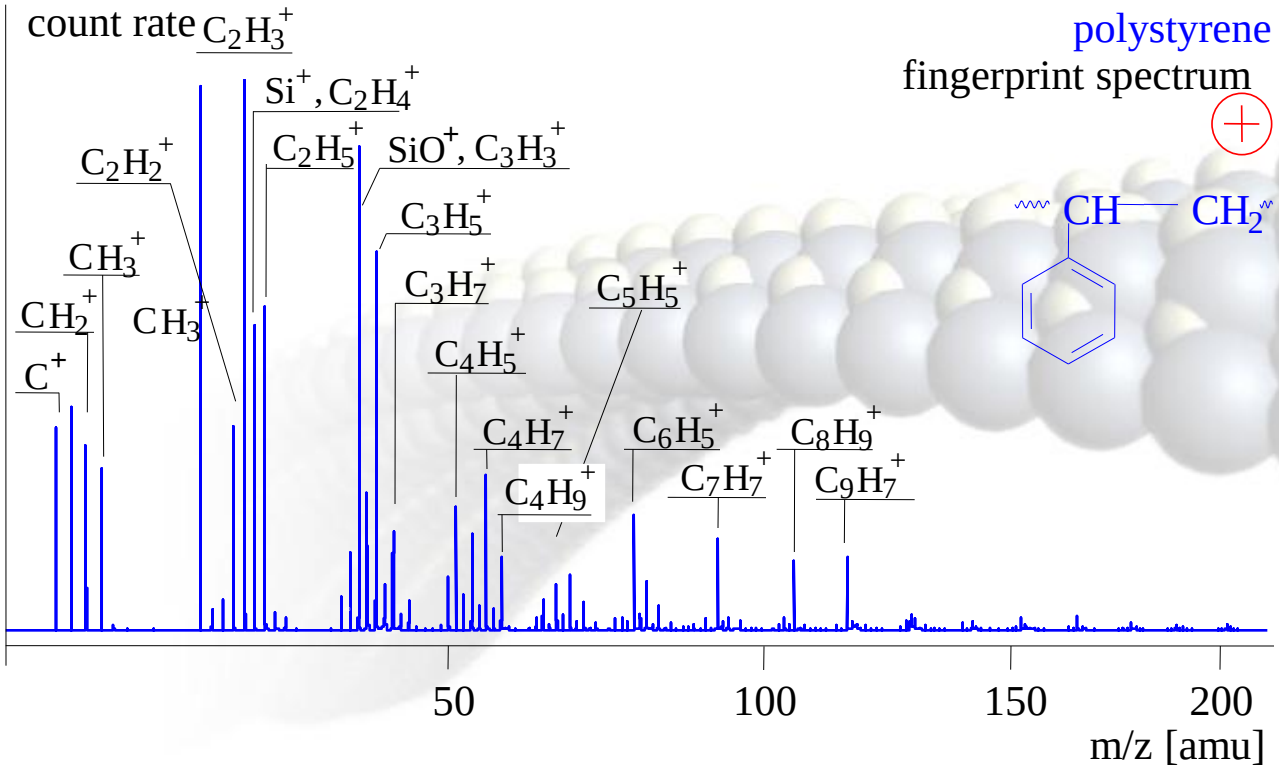

puls length 59...1888 ps

# Time-of-Flight Seconday Ion Mass Spectrometry (ToF-SIMS)

## – Spectral information –



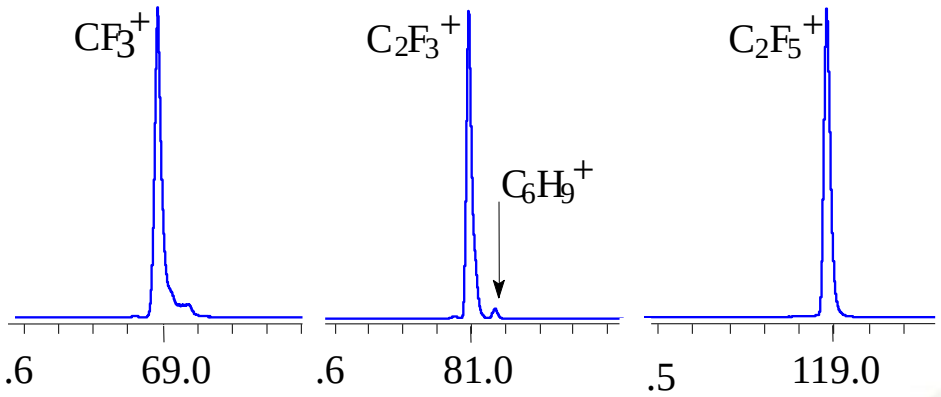
$$E_{kin} = \frac{m}{2} \cdot v^2 = \frac{m}{2} \cdot \left[\frac{s}{t}\right]^2$$



# Time-of-Flight Seconday Ion Mass Spectrometry (ToF-SIMS)

## – Excellent mass resolution – PTFE after its treatment in a hydrogen plasma –

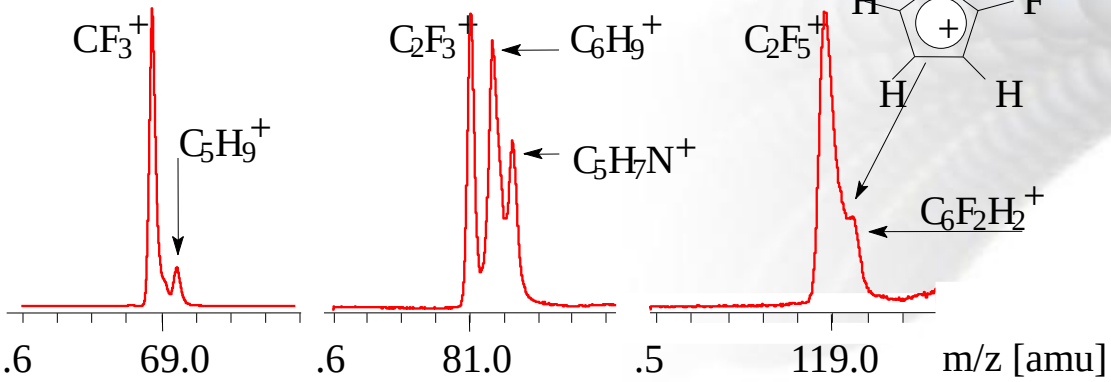
unmodified PTFE




| m/z | measured $m_m$ | calculated $m_c$ | $\Delta = \lvert m_m - m_c \rvert$ |
|---|---|---|---|
| $CF_3^+$ | 68.9873 | 68.9952 | 0.0079 |
| $C_5H_9^+$ | 69.0695 | 69.0717 | 0.0022 |
| $C_2F_3^+$ | 80.9888 | 80.9952 | 0.0064 |
| $C_6H_9^+$ | 81.0645 | 81.0717 | 0.0072 |
| $C_2F_5^+$ | 118.9858 | 118.9920 | 0.0062 |
| $C_6H_9F_2^+$ | 119.0659 | 119.0685 | 0.0026 |

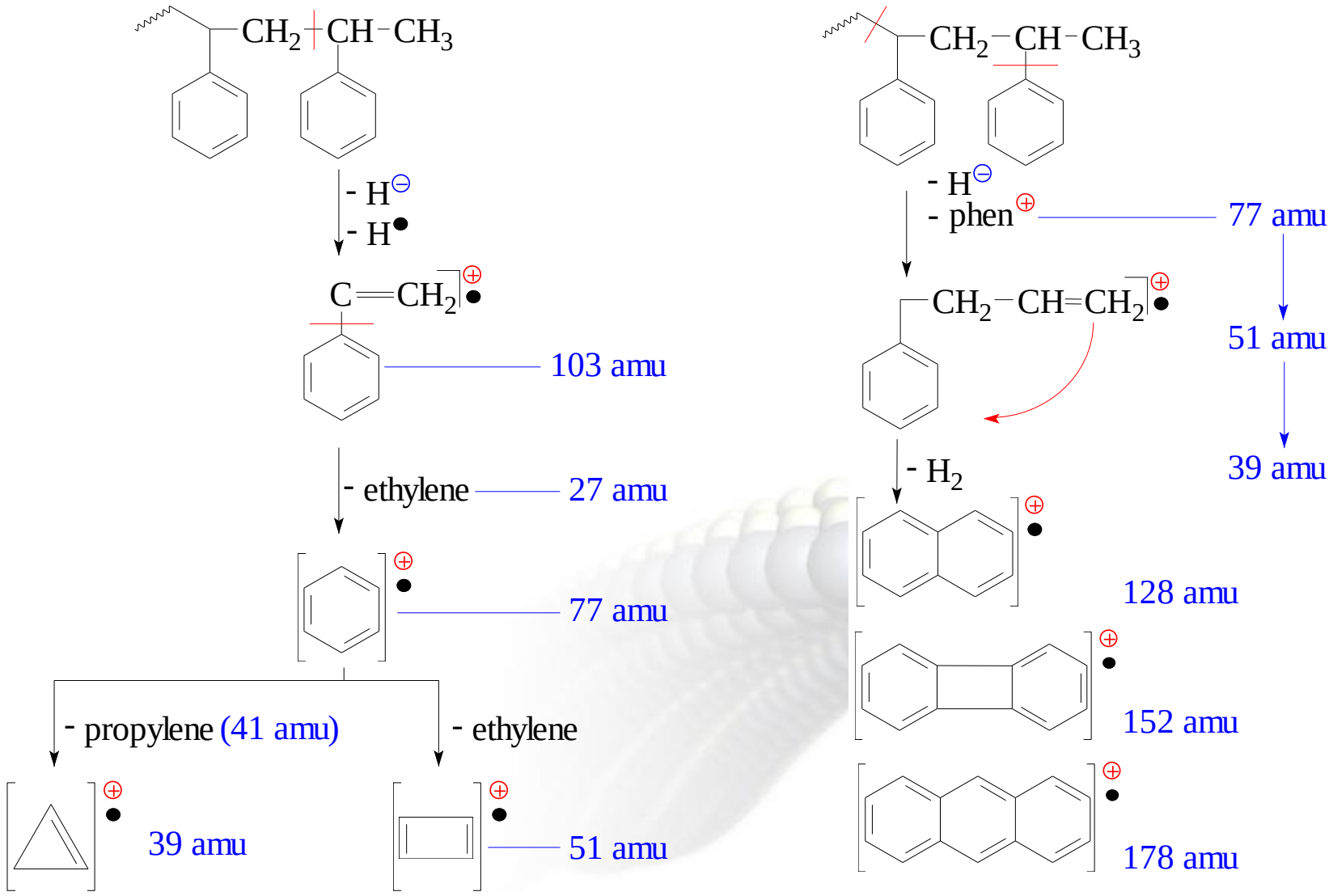
All values were given in [amu]

plasma-treated PTFE



# Fragmentation mechanisms

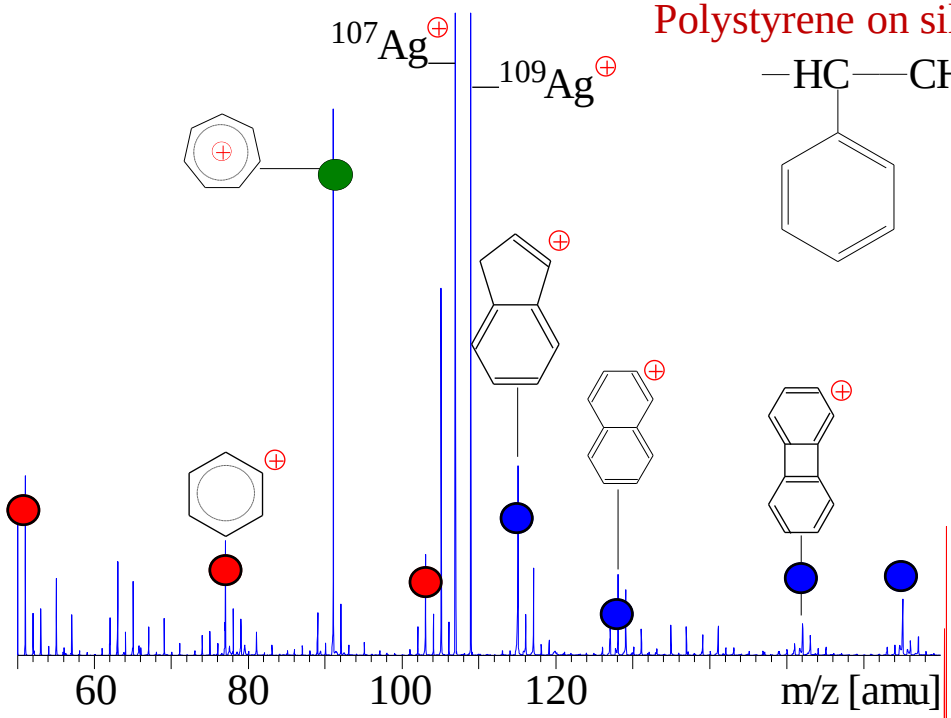
## – e.g. Polymers with aromatic units –

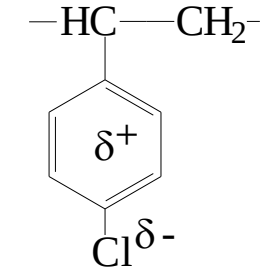


# Fragmentation mechanisms

## – e.g. Polymers with aromatic units –

Polystyrene on silver substrate

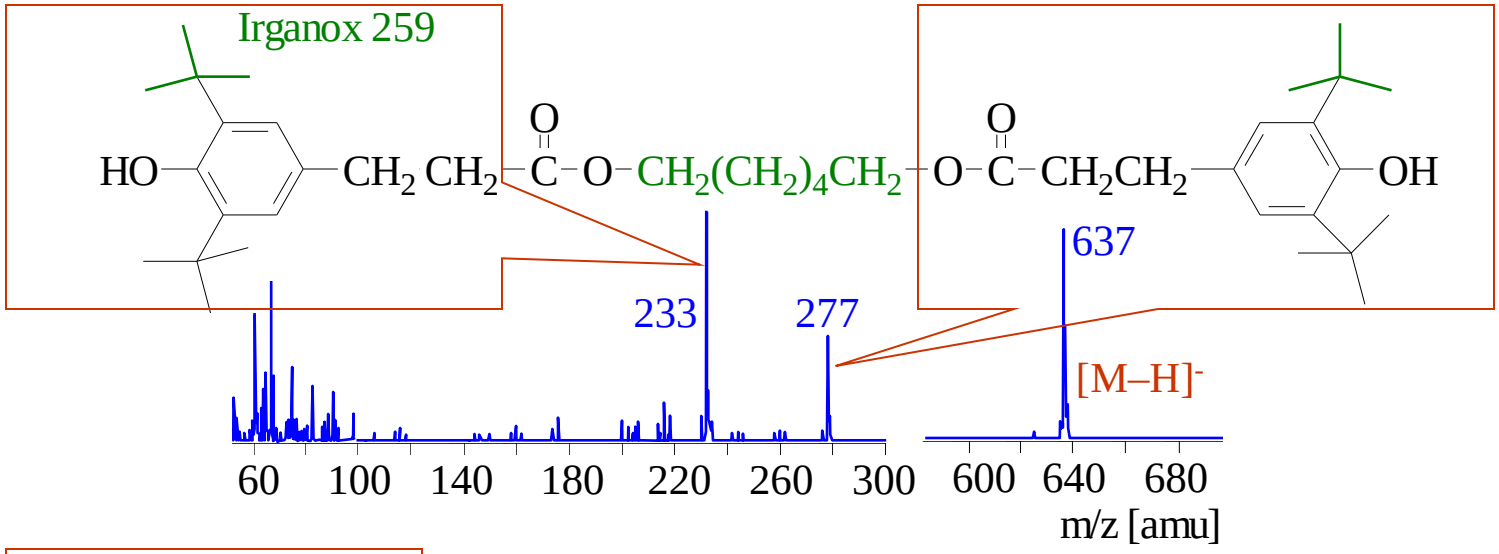


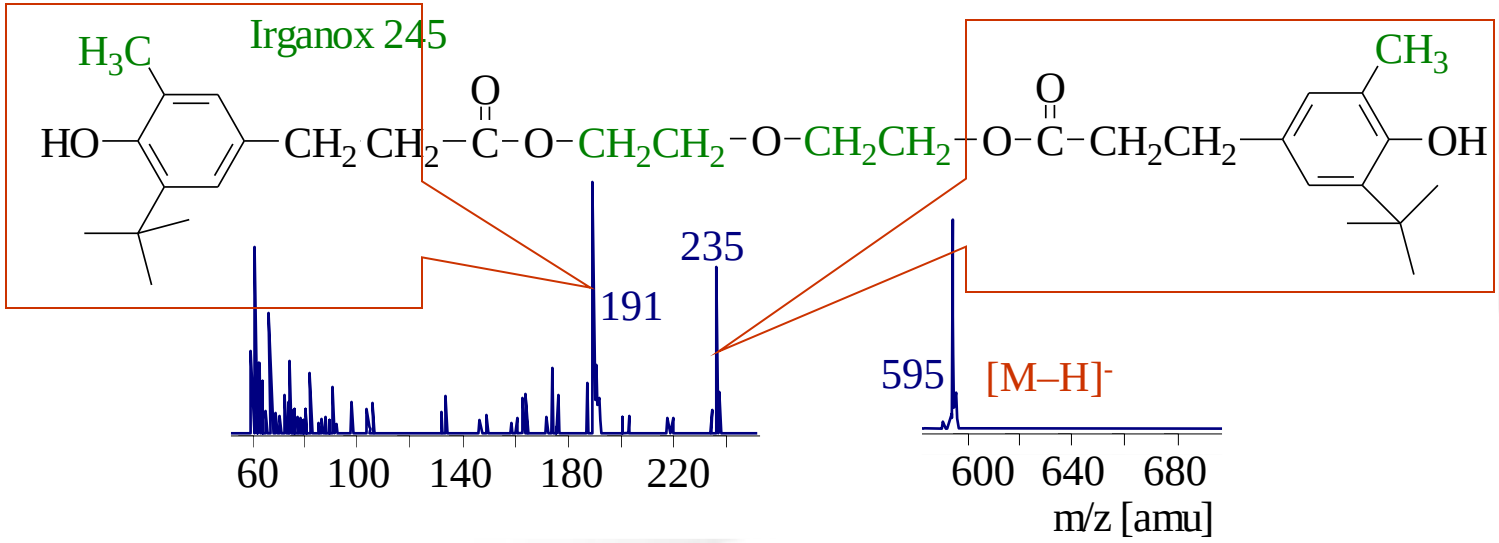




Poly(4-chloro styrene)

# Analysis of additives in polymers

## – No chance for XPS –

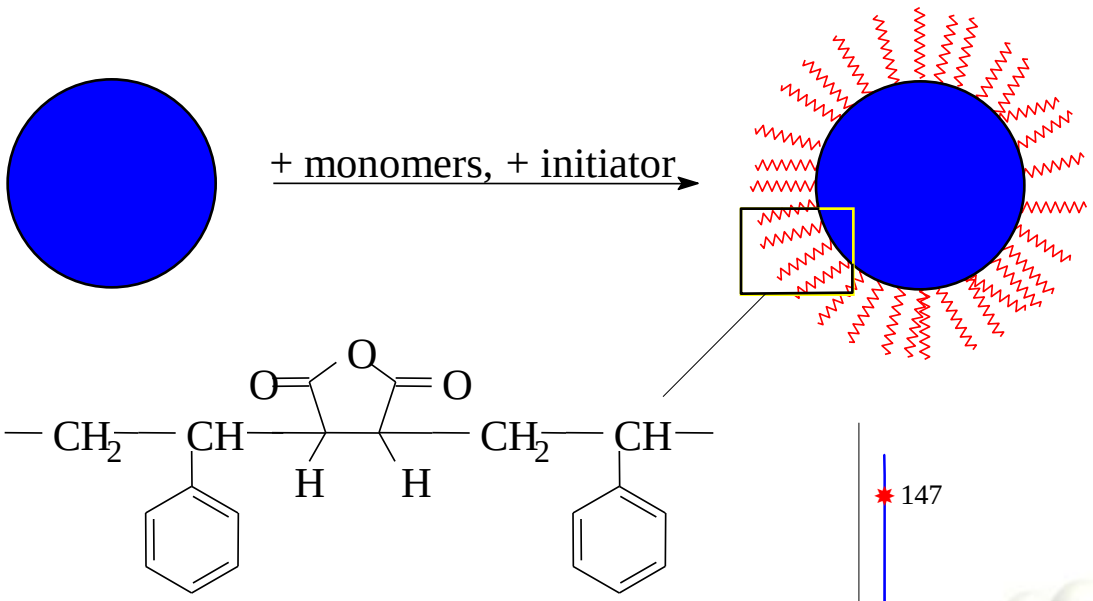


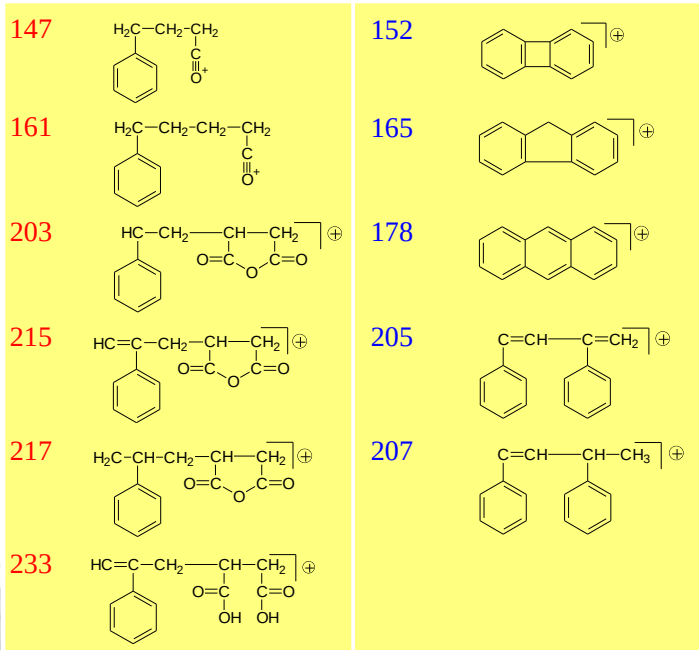




**Analysis of additives, impurities, modifiers etc.**

# Application note of ToF-SIMS

## – Grafting of styrene and maleic anhydride on polyolefin surfaces –

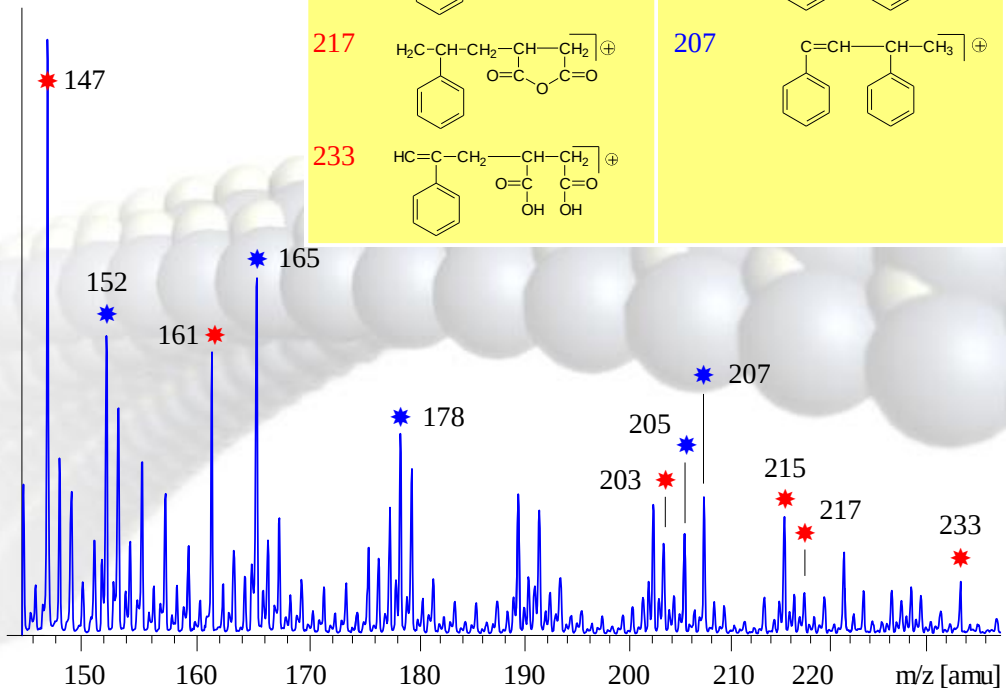



There are polystyrene sequences [Sty-Sty-Sty] ? ☺

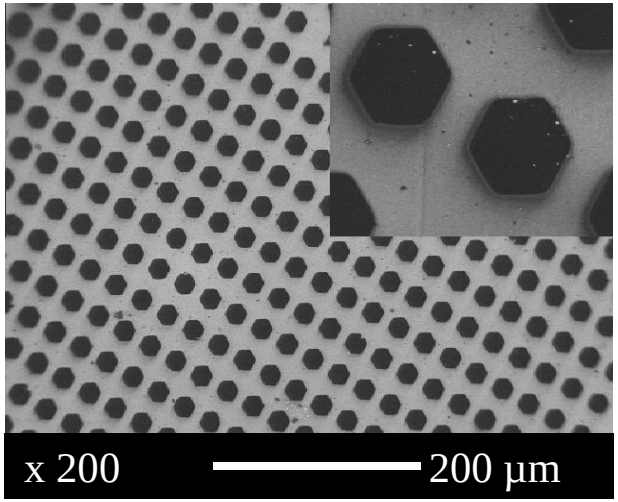
There are maleic anhydride sequences [MSA-MSA-MSA] ? ☹

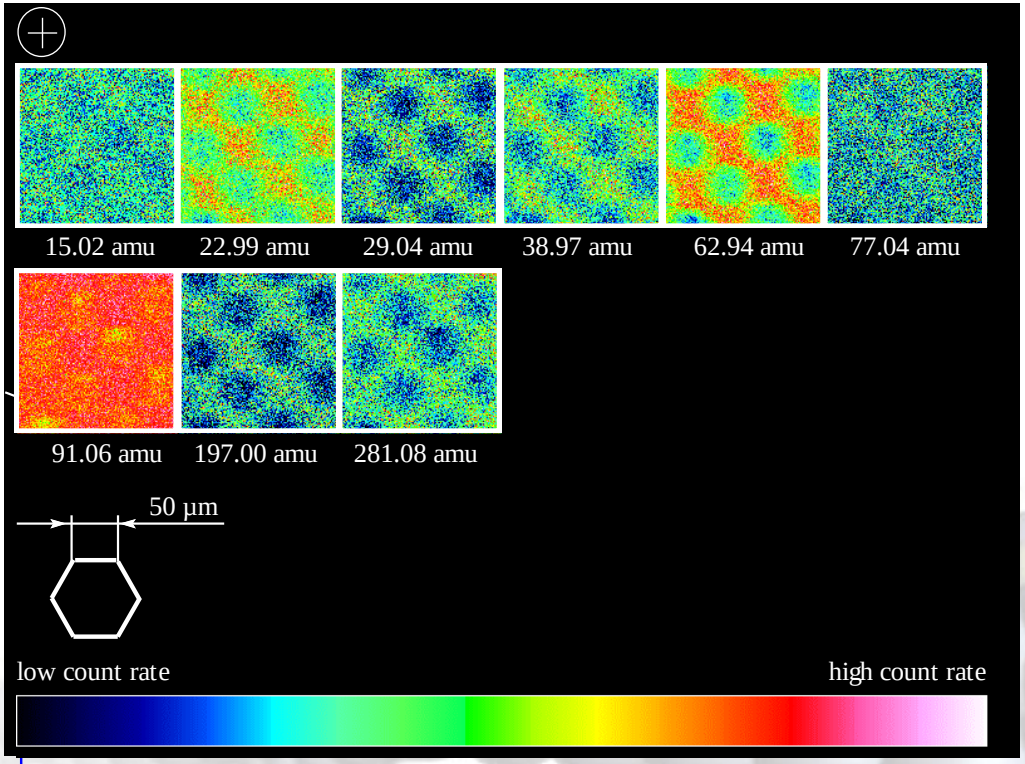
There are hydrolyzed maleic anhydride groups? ☺

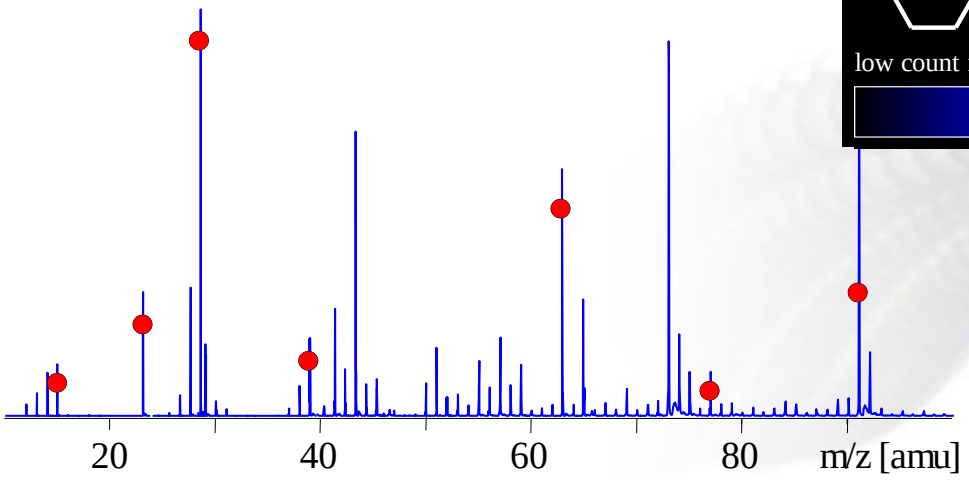


# Imaging-ToF-SIMS

## – Laterally structured poly(γ-benzyl glutamate) –

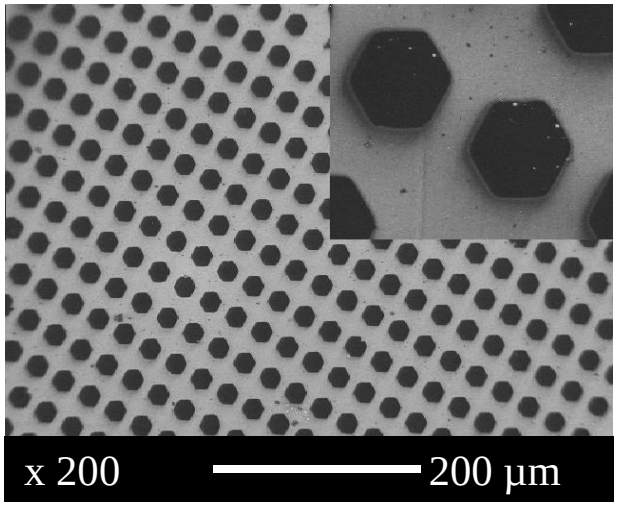


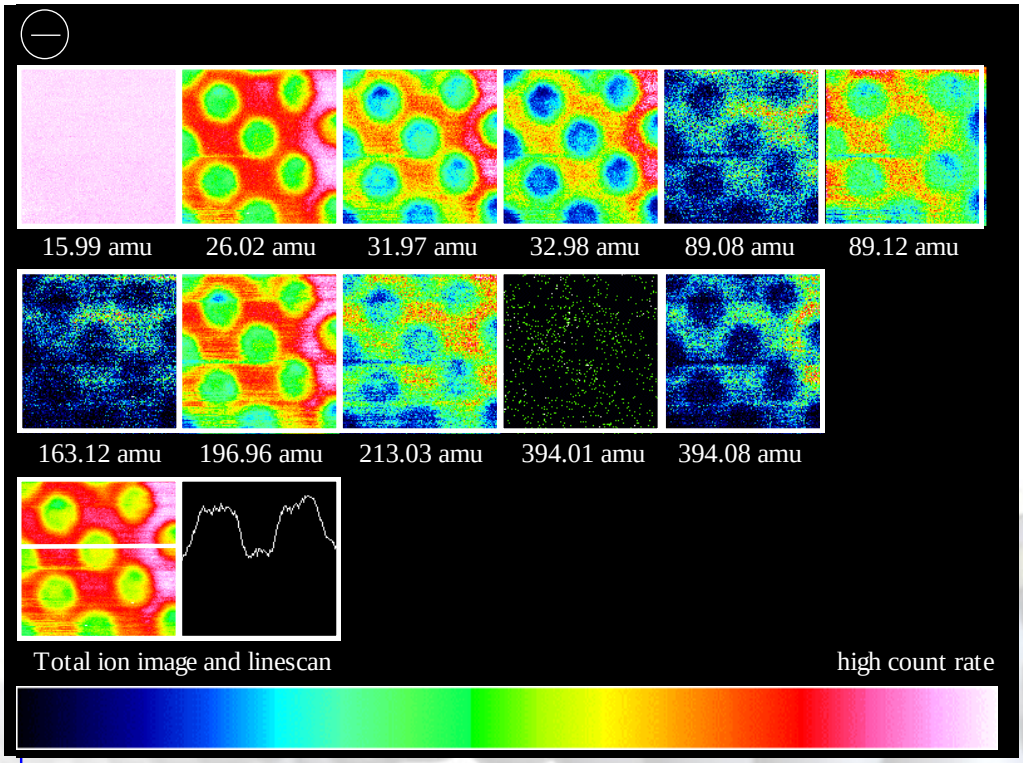



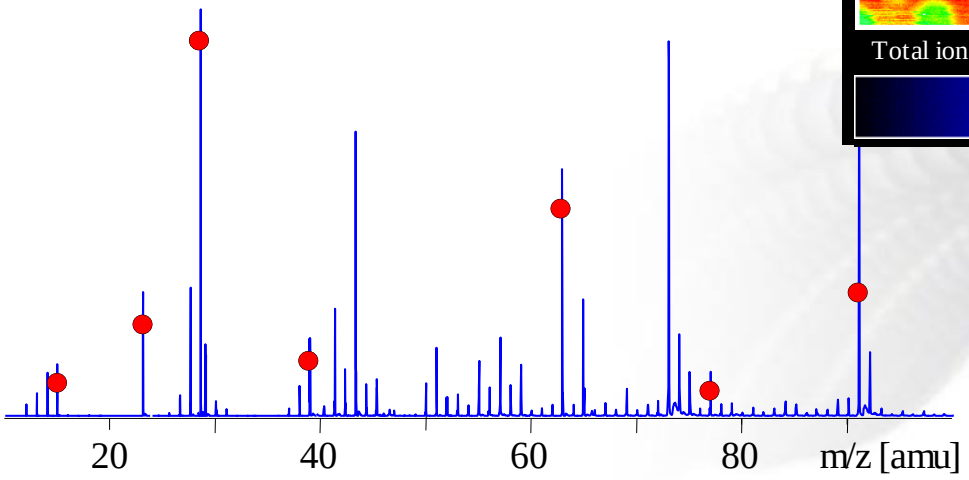



# Imaging-ToF-SIMS

## – Laterally structured poly(γ-benzyl glutamate) –



# Summary
## SSIMS [ToF-SIMS]

**SSIMS is a method oriented to detect and analyse molecules on the surface of samples**

- analysis of molecule species [chemical structure and mass of the polymer's repeating units ⇨ type of monomer
- **non**-quantitative surface analysis [semi-quantitative surface analysis],
- analysis of end groups Endgruppen ⇨ **determination of molar masses and molar mass distributions** on surfaces
- analysis of additives, impurities, modifiers etc. [**traces can be detected**],
- analysis of structural changes caused by surface mofication, functionalization, and aging.