Surface Chemical Analysis by XPS and SIMS

- a means to one's ends or an end to one's means?

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www.ncl.ac.uk/nexus

Surface Chemical Analysis by XPS and SIMS

- a means to one's ends or an end to one's means?

Outline:

- **SEAL**
- **XPS and SIMS**
- **What information is available?**
- **Examples**
- **Conclusions**

Surface Chemical Analysis by XPS and SIMS

- a means to one's ends or an end to one's means?

The Surface Engineering and Analysis Laboratory - SEAL

SEAL

NEXUS
National EPSRC XPS Users' Service

New Ion Beam Tools
- ToFSIMS
- Helium Ion

Surface Chemical Analysis by XPS and SIMS

- a means to one's ends or an end to one's means?

An end to one's means?

- tendency to avoid surface analysis because it is too expensive
- commercial charges up to £3000 per day
- EPSRC Mid-range XPS facility at Newcastle – 'NEXUS'
  free to EPSRC *fundable* researchers
- SEAL Ion Beam Tools
  may need to make a small charge to cover running costs
- SEAL has the best instrument base for surface analysis in Europe including XPS, ToFSIMS, Gas Cluster Ion Beams and Helium Ion Microscopy facilities

Surface Chemical Analysis by XPS and SIMS

- a means to one's ends or an end to one's means?

An end to one's means?

- not here!

- means to one's ends …………….

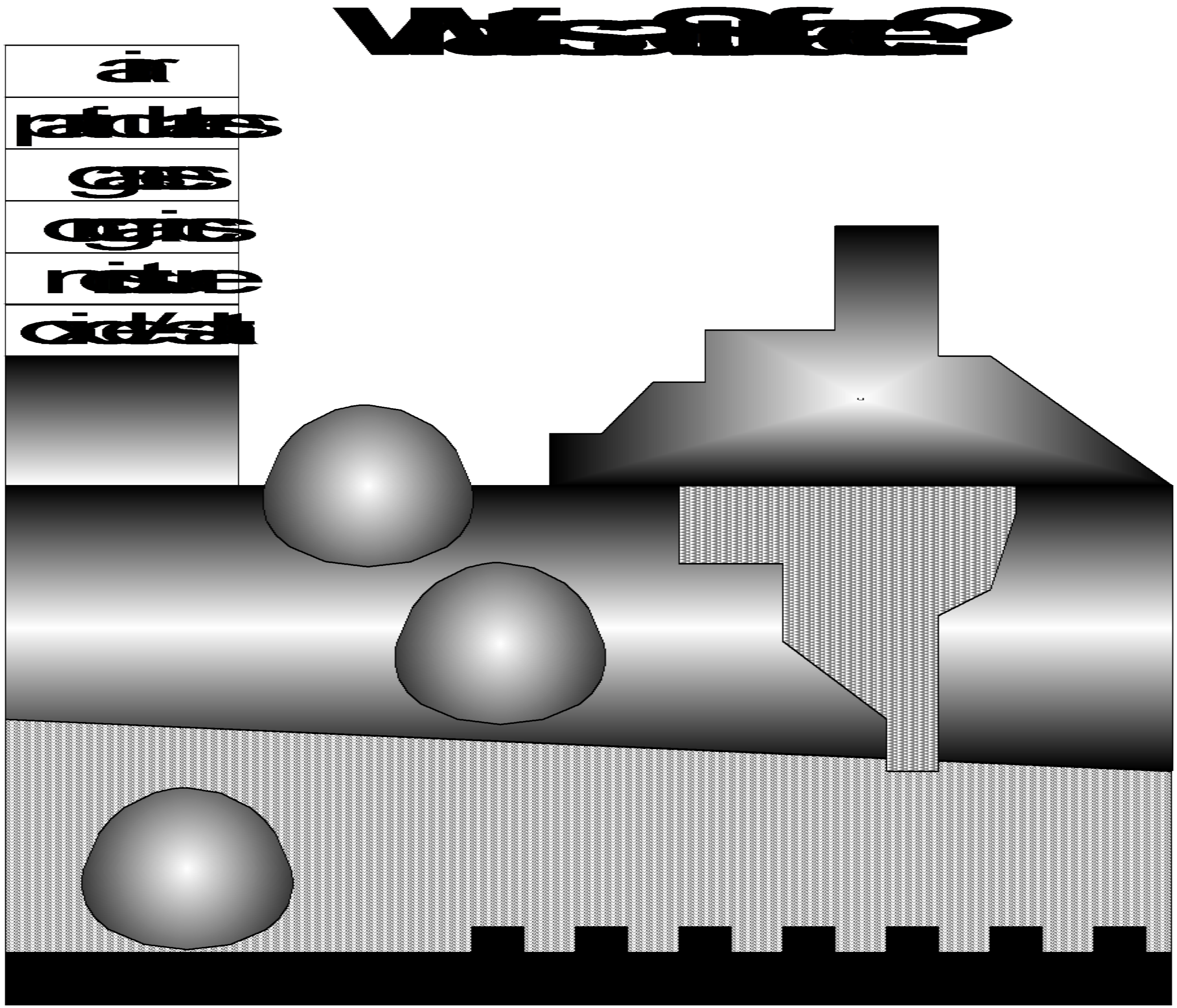
What can we do?

- determine the elemental, chemical and molecular composition of the outermost surface regions of organic and inorganic materials using spectroscopy, imaging and depth profiling

How do we do it?

- X-Ray Photoelectron Spectroscopy, XPS or ESCA
- Static Secondary Ion Mass Spectrometry, SSIMS
- Dynamic Secondary Ion Mass Spectrometry, DSIMS

Surface Chemical Analysis by XPS and SIMS



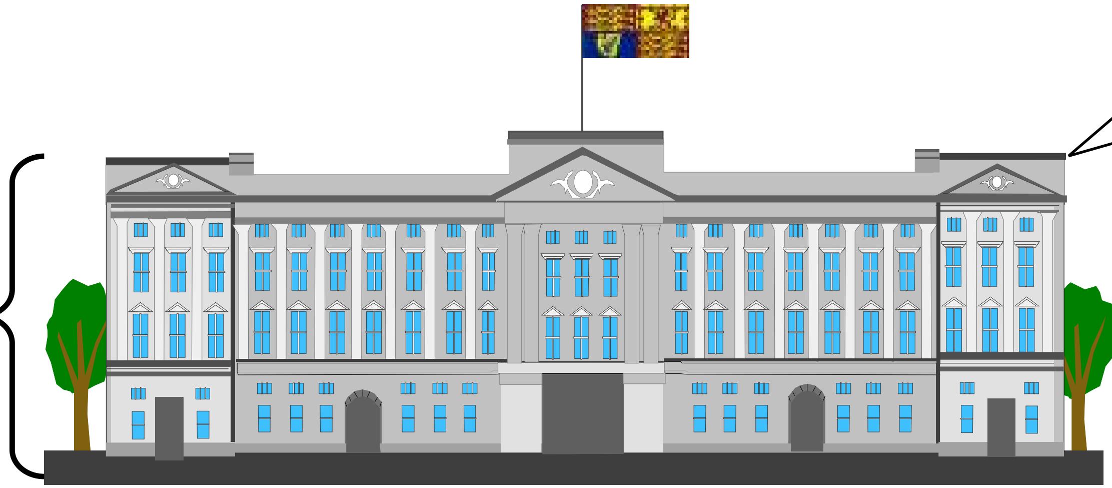
What is a surface?

Sampling Depths

SEM / EDX
IR / Raman

SSIMS ~1nm
XPS ~10nm

~1μm



1-10 nm

Surface Chemical Analysis by XPS and SIMS

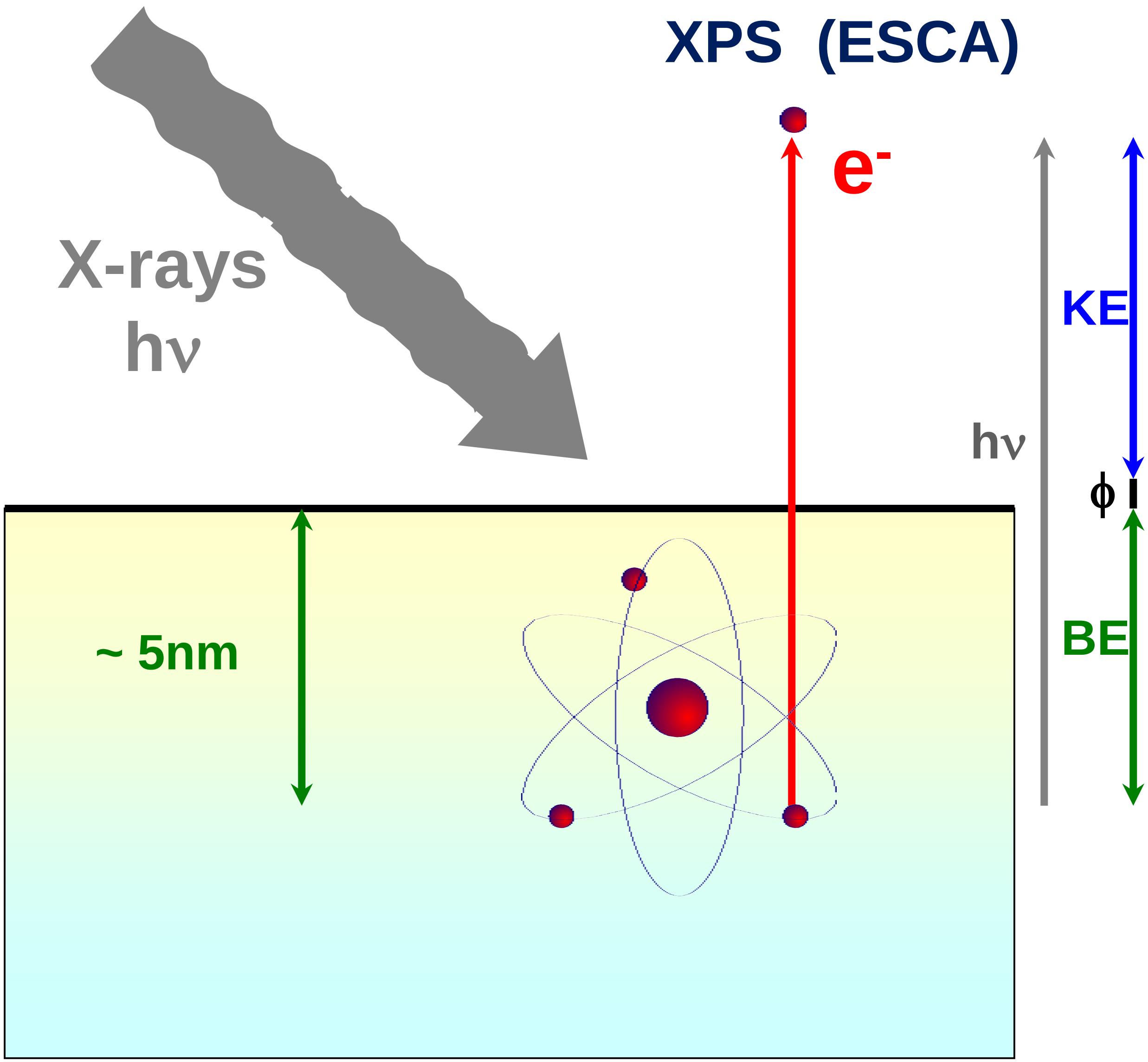
Real surfaces are rarely pure materials!

Surface	≠	Bulk material
Segregation		Surface Engineering
Migration		coatings
Phase Separation		treatment
Crystallinity		flame, plasma, EB
MW		chemical
Contamination		Adsorption
Degradation		Corrosion
tribology		Oxidation
heat, light etc		Hydrolysis
chemical		

What is on there?

- Surfactants
- Anti-oxidants
- Lubricants / slip agents
- Mould Release agents
- Inorganics
- 'Contaminants'
- Reaction / Process deposits
- Polymers
- Resins
- Biomaterials
- Oligomers
- etc.

XPS (ESCA)



$h\nu = KE + BE + \phi$

$KE = h\nu - BE - \phi$

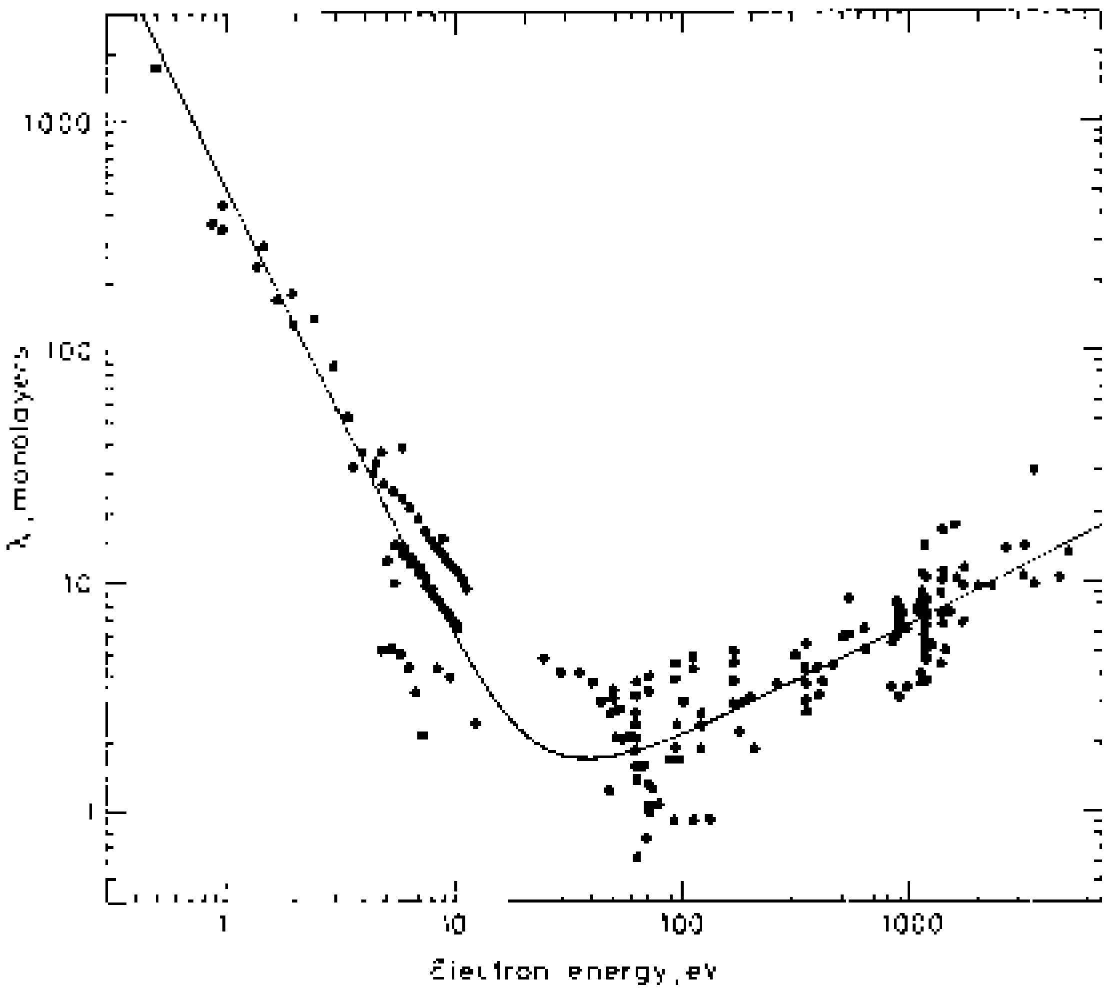
$BE = h\nu - KE - \phi$

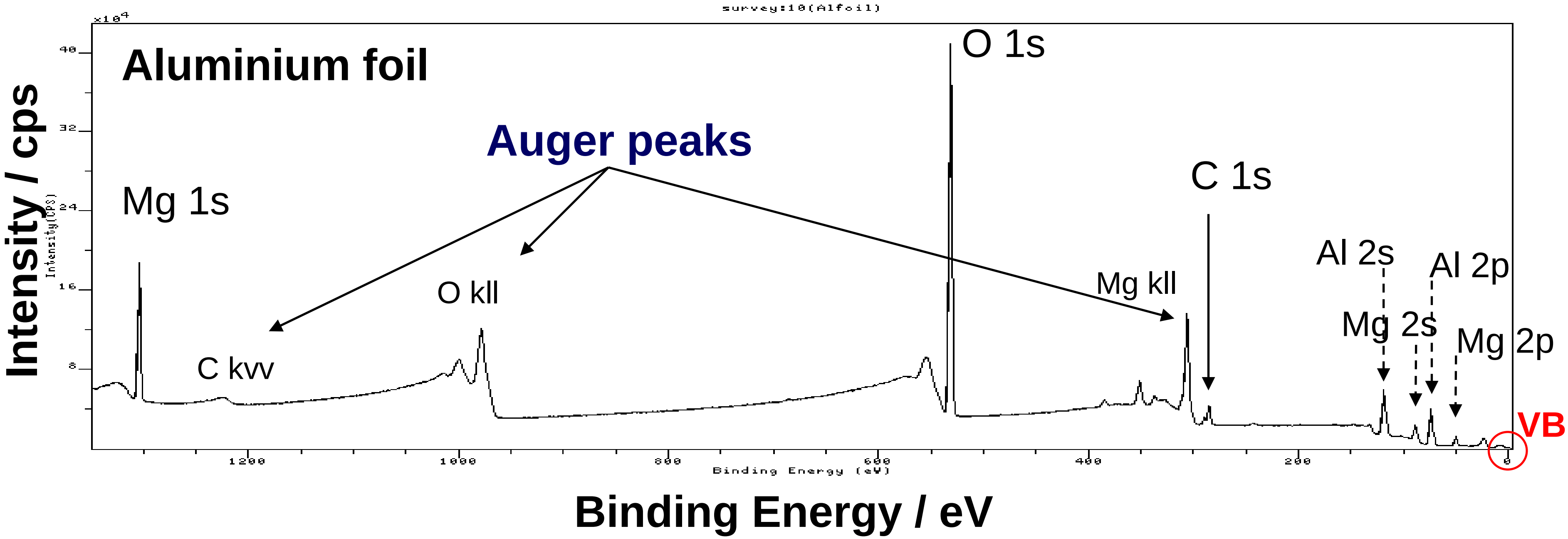
Kinetic Energy

Binding Energy

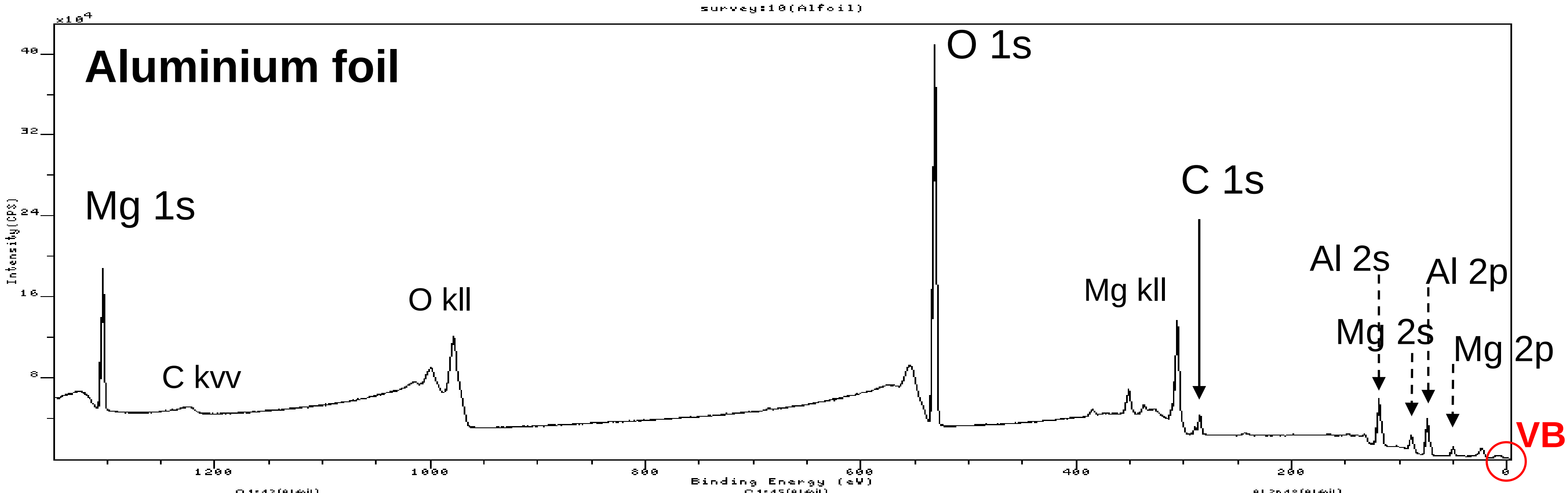
Surface Chemical Analysis by XPS and SIMS

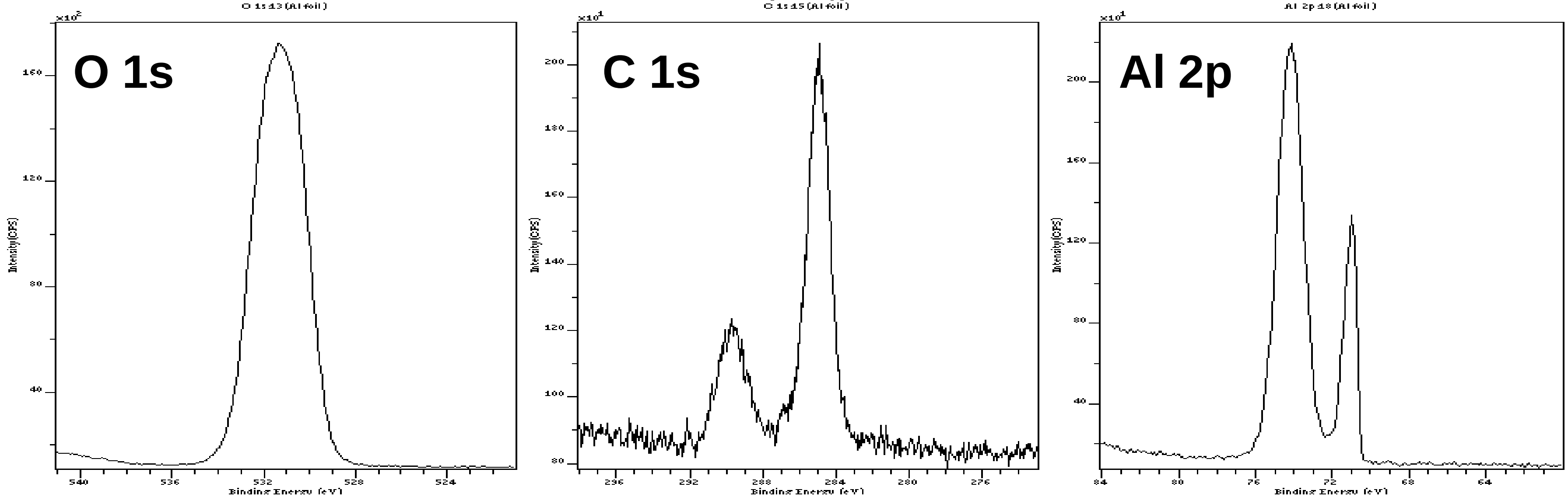
λ vs photoelectron KE




survey:10(Alfoil)
Aluminium foil
Auger peaks
O 1s
C 1s
Mg 1s
O kll
Mg kll
C kvv
Al 2s
Al 2p
Mg 2s
Mg 2p
VB
Intensity / cps
Binding Energy / eV

Surface Chemical Analysis by XPS and SIMS





Surface Chemical Analysis by XPS and SIMS

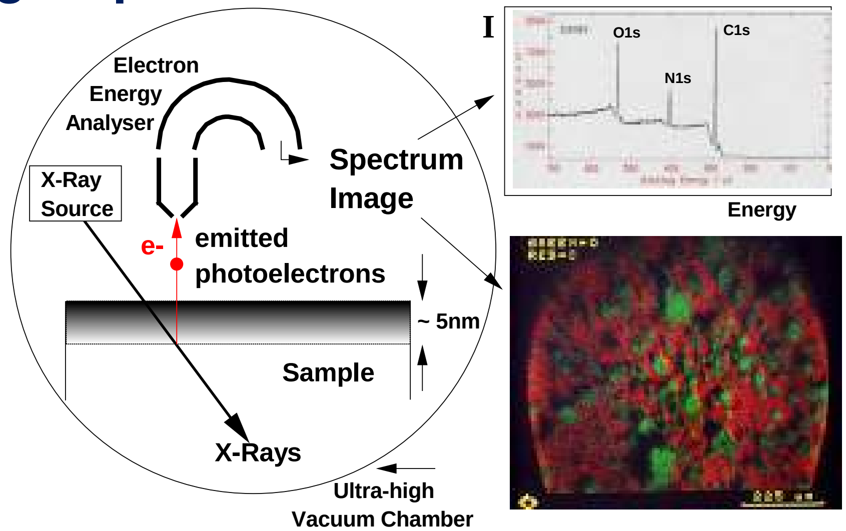
XPS (ESCA)

X-ray Photoelectron Spectroscopy

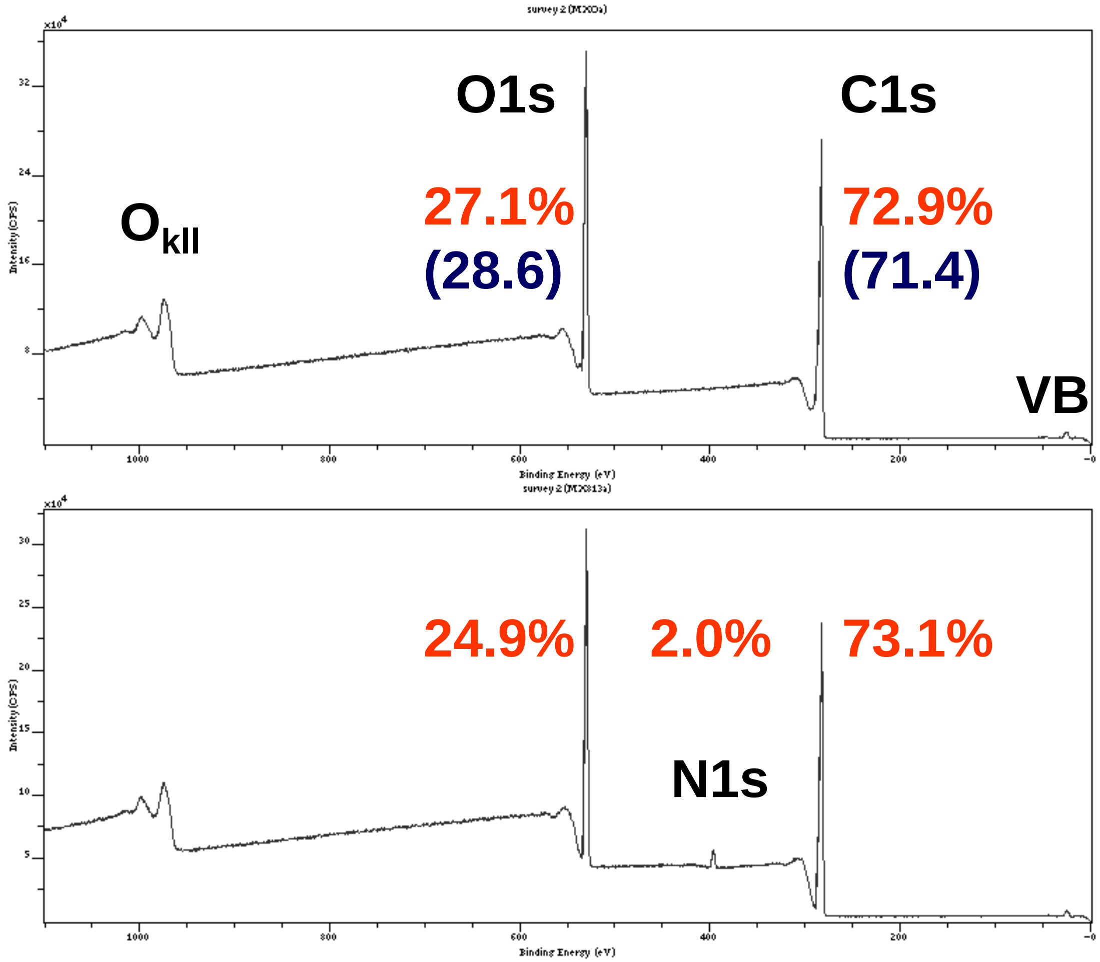
- detects all elements except H
- detects 1 atom in 1000
- sampling depth from ~ 1nm to ~ 10nm
- relative quantification of elements and chemistry
- chemical information ⇒ bonding, oxidation state, functional groups etc.

- 1-D linescans
- 2-D imaging at ~ 2μm resolution
- 3-D depth profiles

- solids and liquids
- electrical conductors and insulators
- analysis at -150°C up to 600°C
- automation



Surface Chemical Analysis by XPS and SIMS

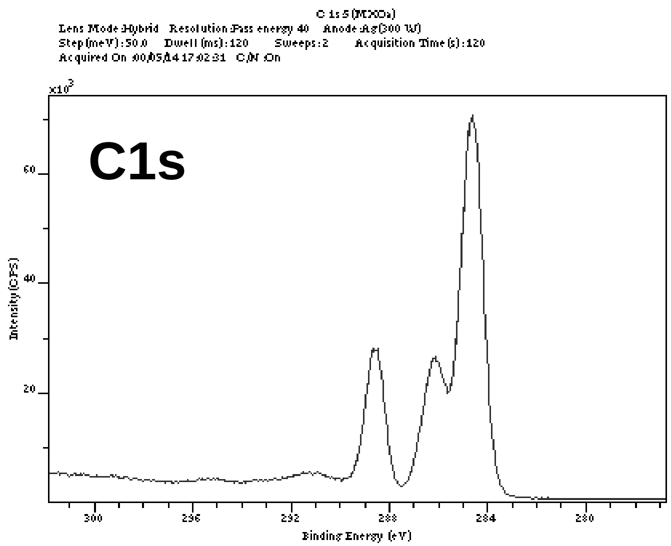


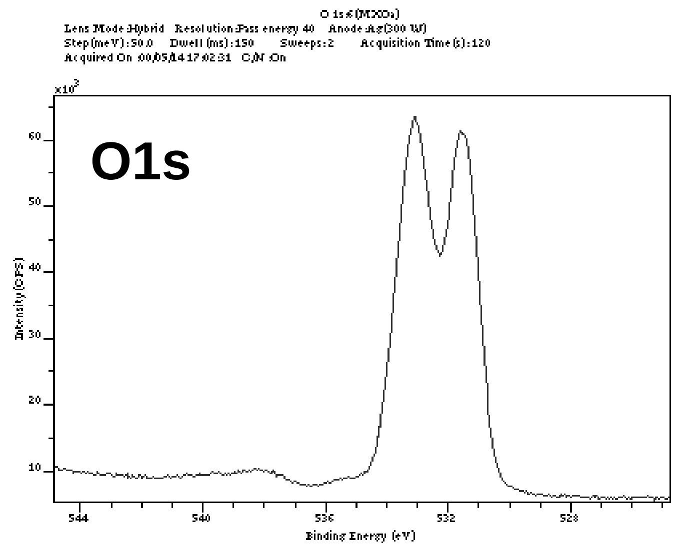
PET

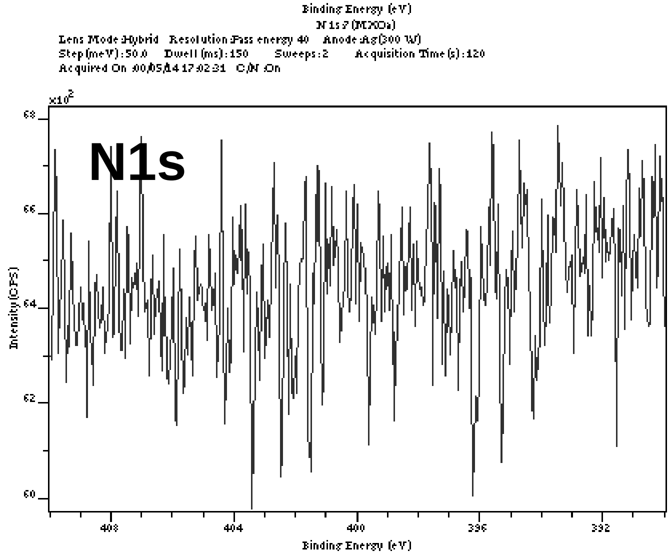
coating

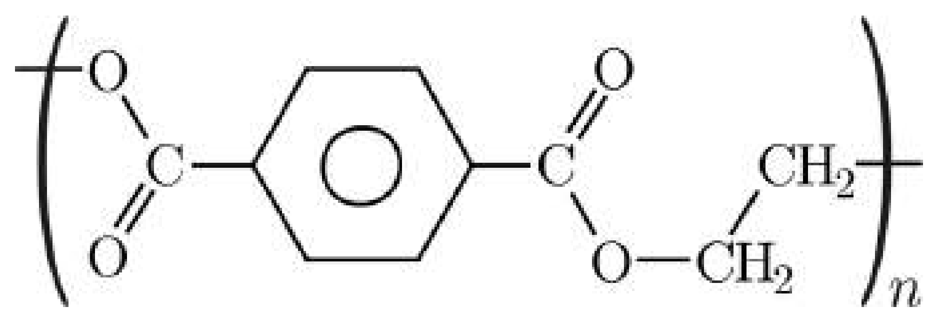
Relative Atomic Percentage Compositions - number density

Surface Chemical Analysis by XPS and SIMS



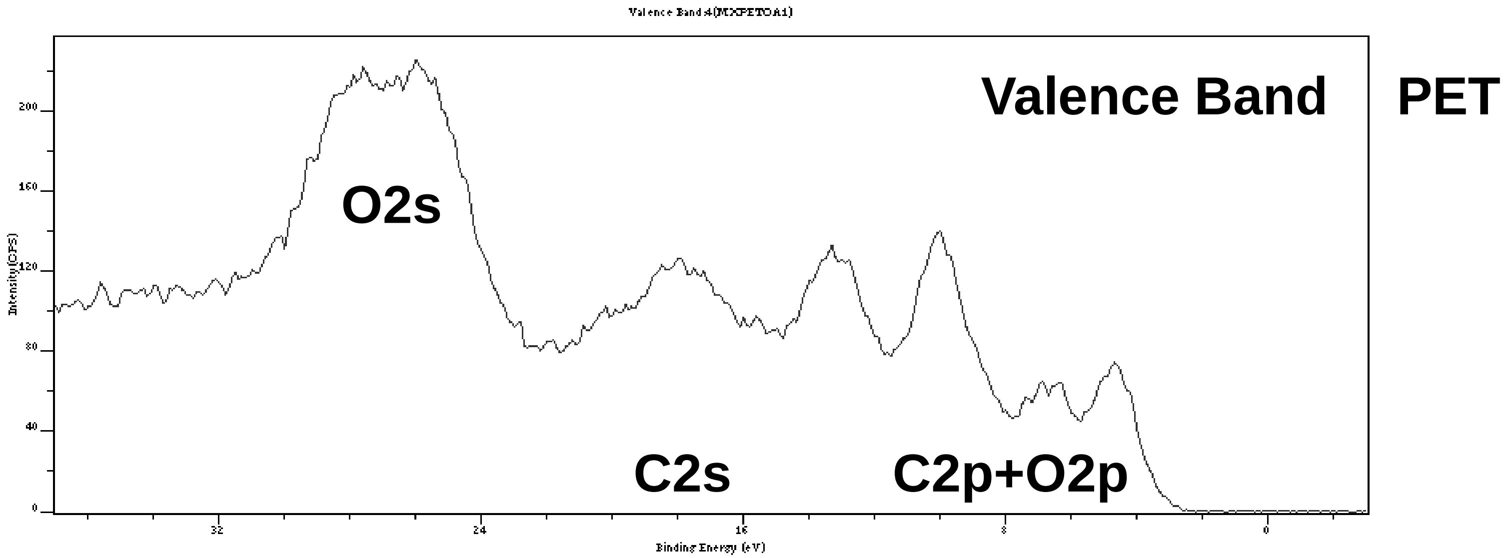


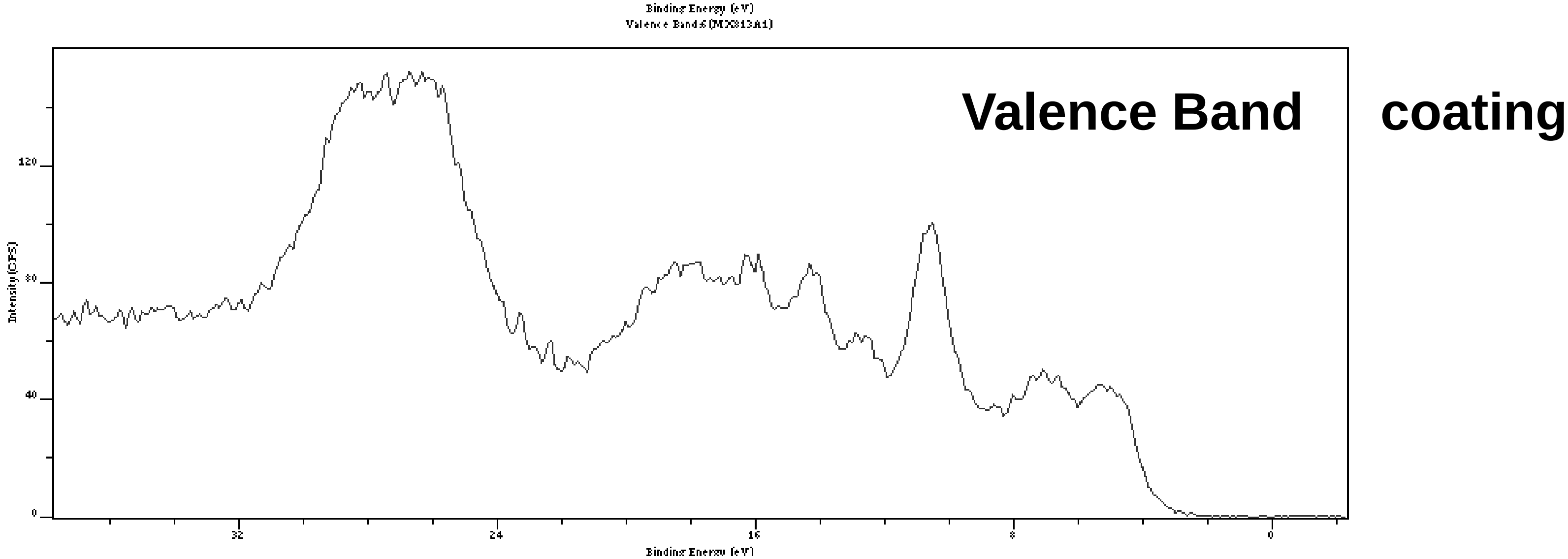




PET

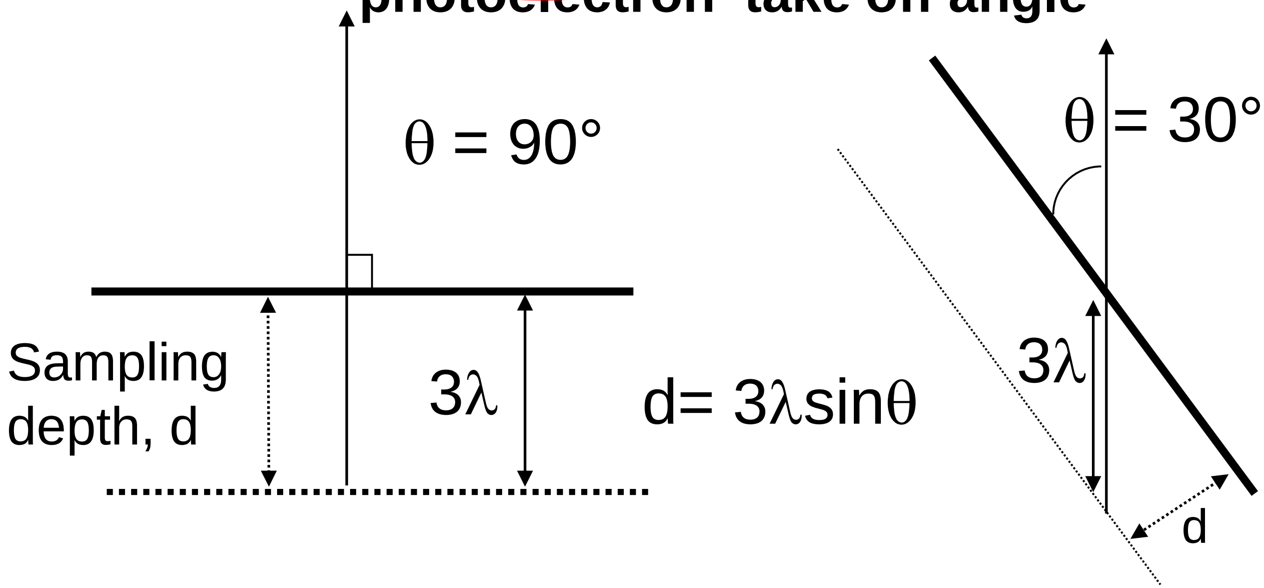
Surface Chemical Analysis by XPS and SIMS





Angle resolved XPS

Tilt the sample to change the photoelectron 'take off angle'



$$I / I_{total} = 1 - e^{-n\lambda}$$

n	% of total signal
1	63.2
2	86.5
3	95.0
4	98.2
5	99.3
6	99.7

λ = inelastic mean free path between collisions, 'imfp'

Typical sampling depths ('3 λ'):

~10nm in organic materials
~5nm in oxides
~3nm in metals

Angle-resolved XPS

- tilt the sample ….. ARXPS

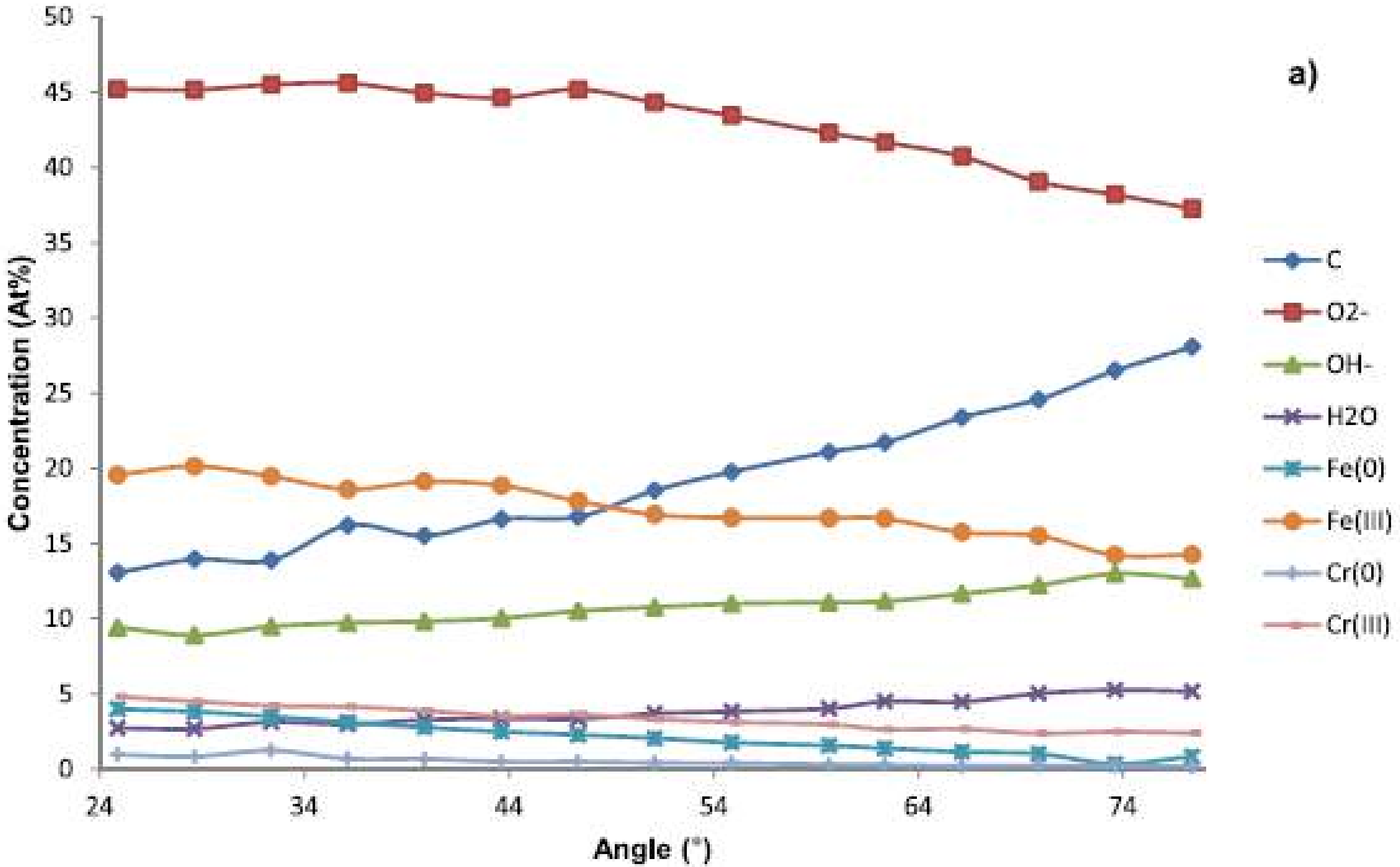
or

- collect photoelectrons leaving the surface from a range of angles at the same time ….. PARXPS

Thermo 'Thetaprobe'

Surface Chemical Analysis by XPS and SIMS

316L Stainless Steel Surface – etched and air exposed



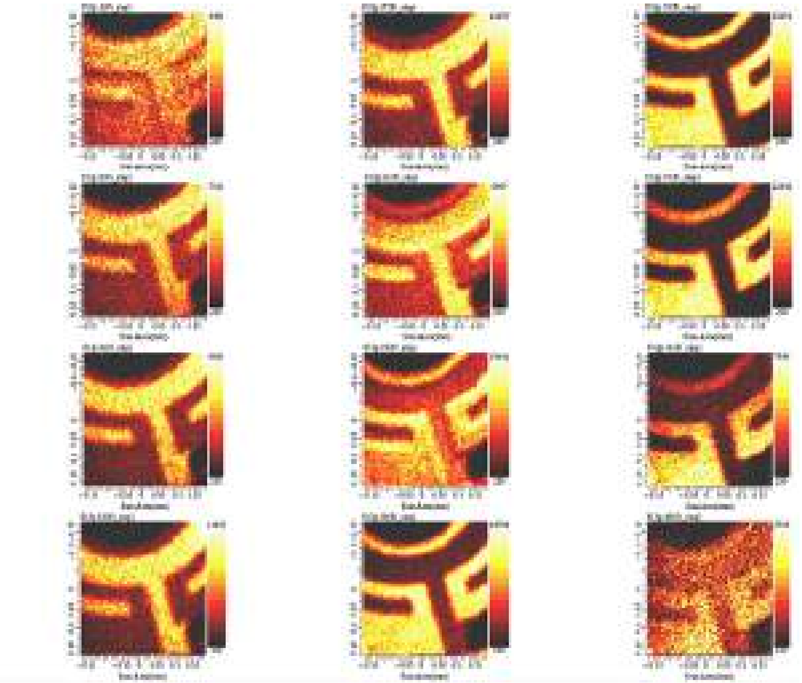
~ 2.5 depth / nm ~1.0

Tardio et al., Comparative study of the native oxide on 316L stainless steel
J. Vac. Sci. Technol. A 33 (5) 2015

Imaging XPS

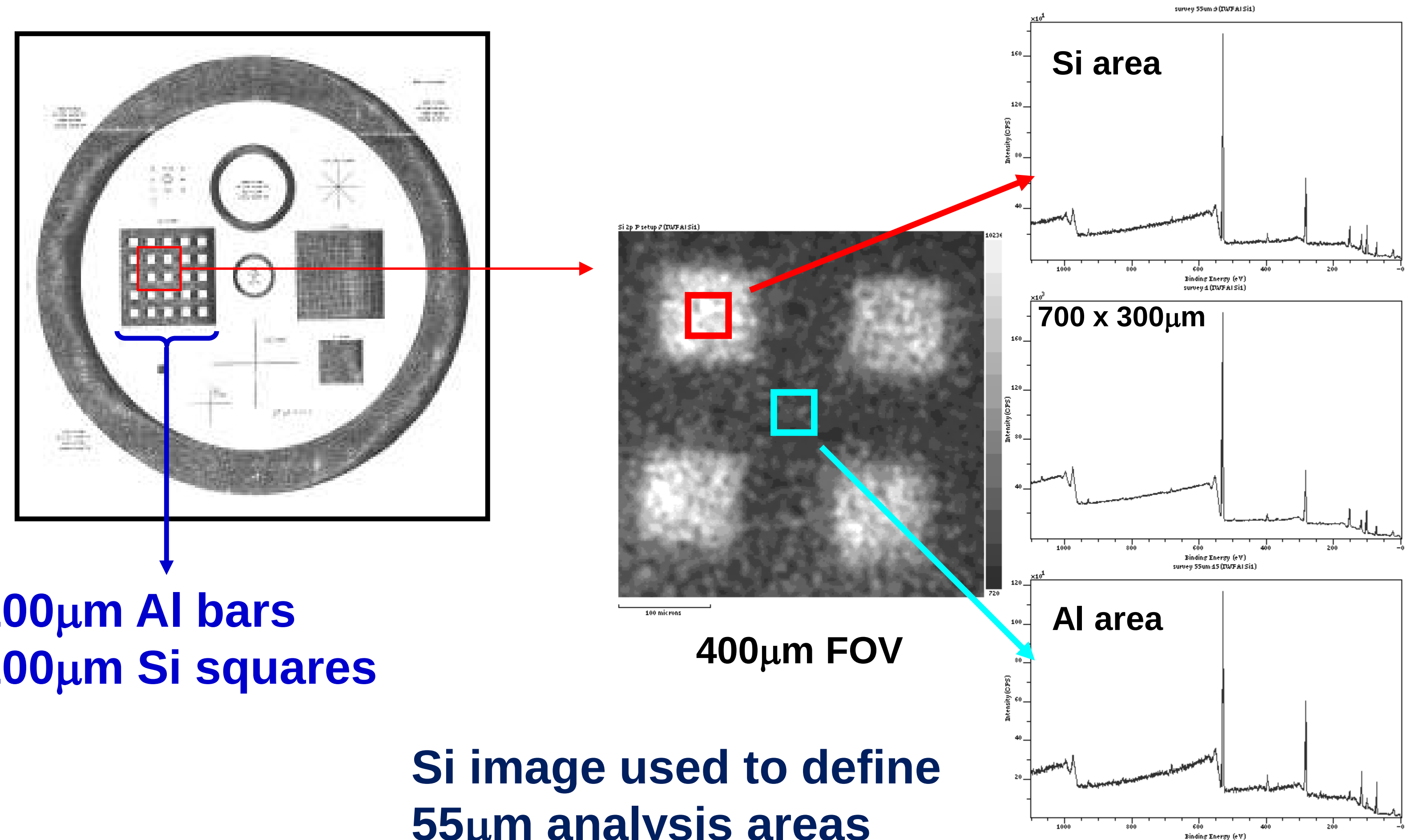
- element and chemical state images
- 2μm spatial resolution

- Useful to align small area spectroscopy



Surface Chemical Analysis by XPS and SIMS

Al on Si SEM test pattern



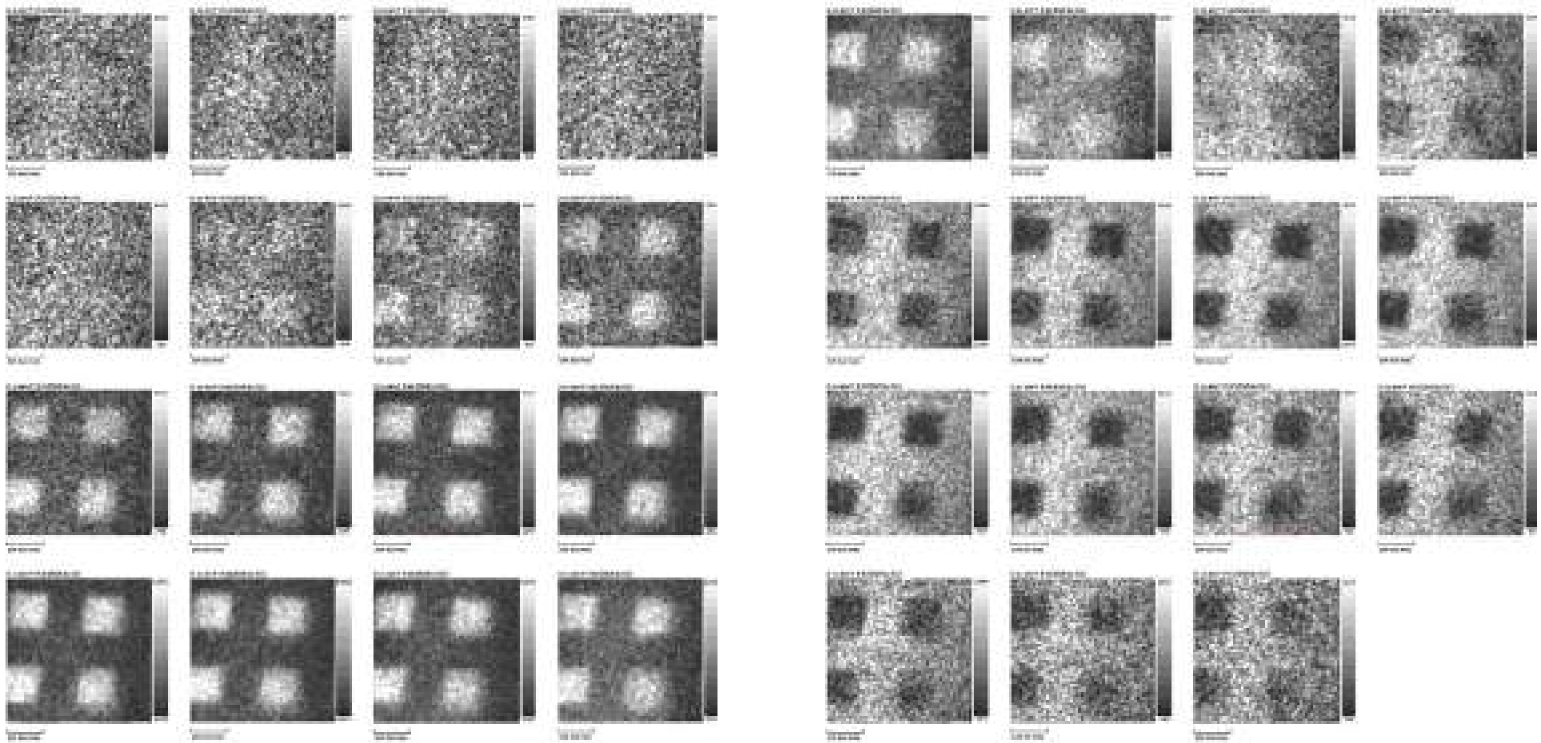
100μm Al bars
100μm Si squares

Si image used to define 55μm analysis areas

Al on Si SEM test pattern - 100μm bars

“Hyperspectral Imaging”

- Record images at different BE’s
- Select area ⇒ regenerate spectra



O1s images 533 - 527eV, 0.2eV step

Secondary Ion Mass Spectrometry – 'SIMS'

'Static' mode	'Dynamic' mode
SSIMS	DSIMS
Low sample damage	High sample damage
'Fingerprint' spectra	Composition depth profiles

Primary Ion Dose Density

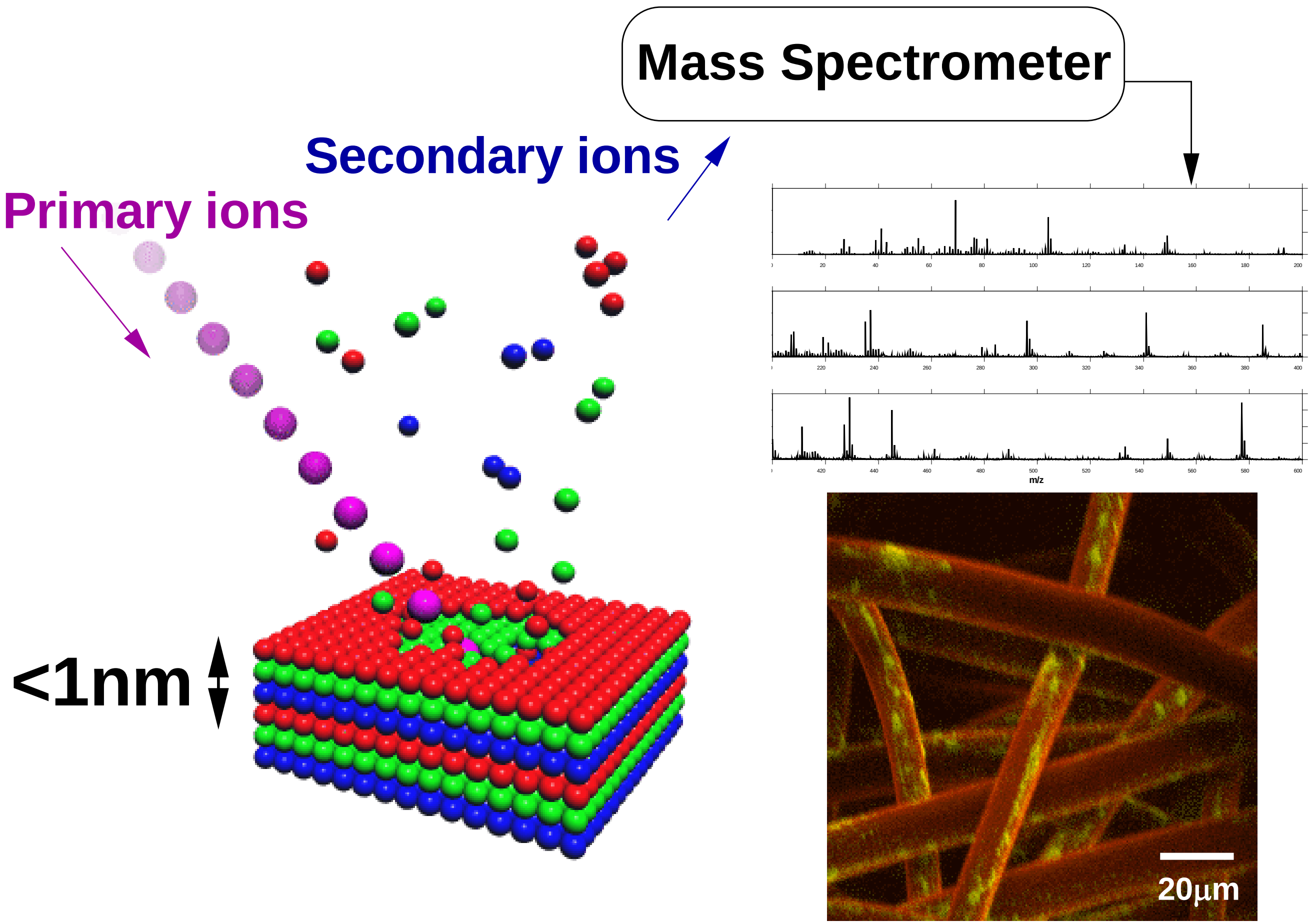
$<1\times10^{12}$ ions cm^{-2}	$>1\times10^{13}$ ions cm^{-2}

Typical surface = 1×10^{15} atoms cm^{-2}

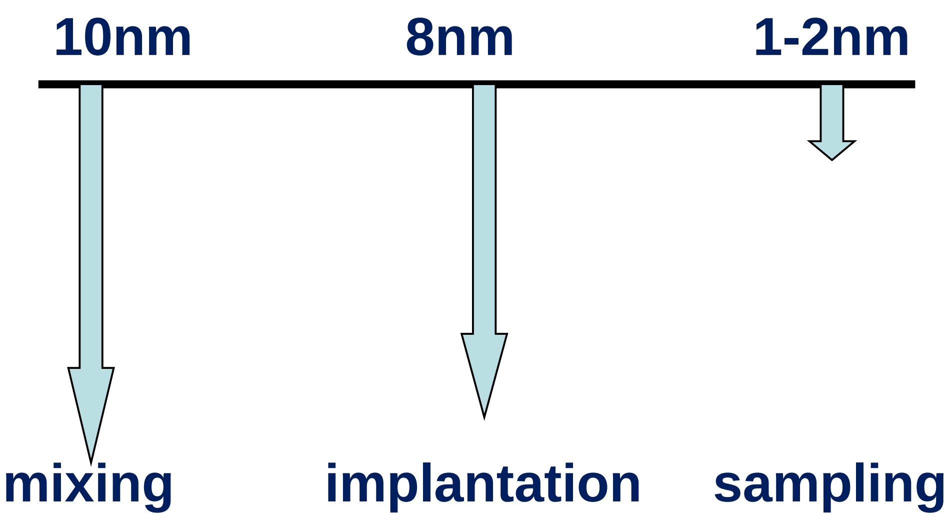
What is SIMS?

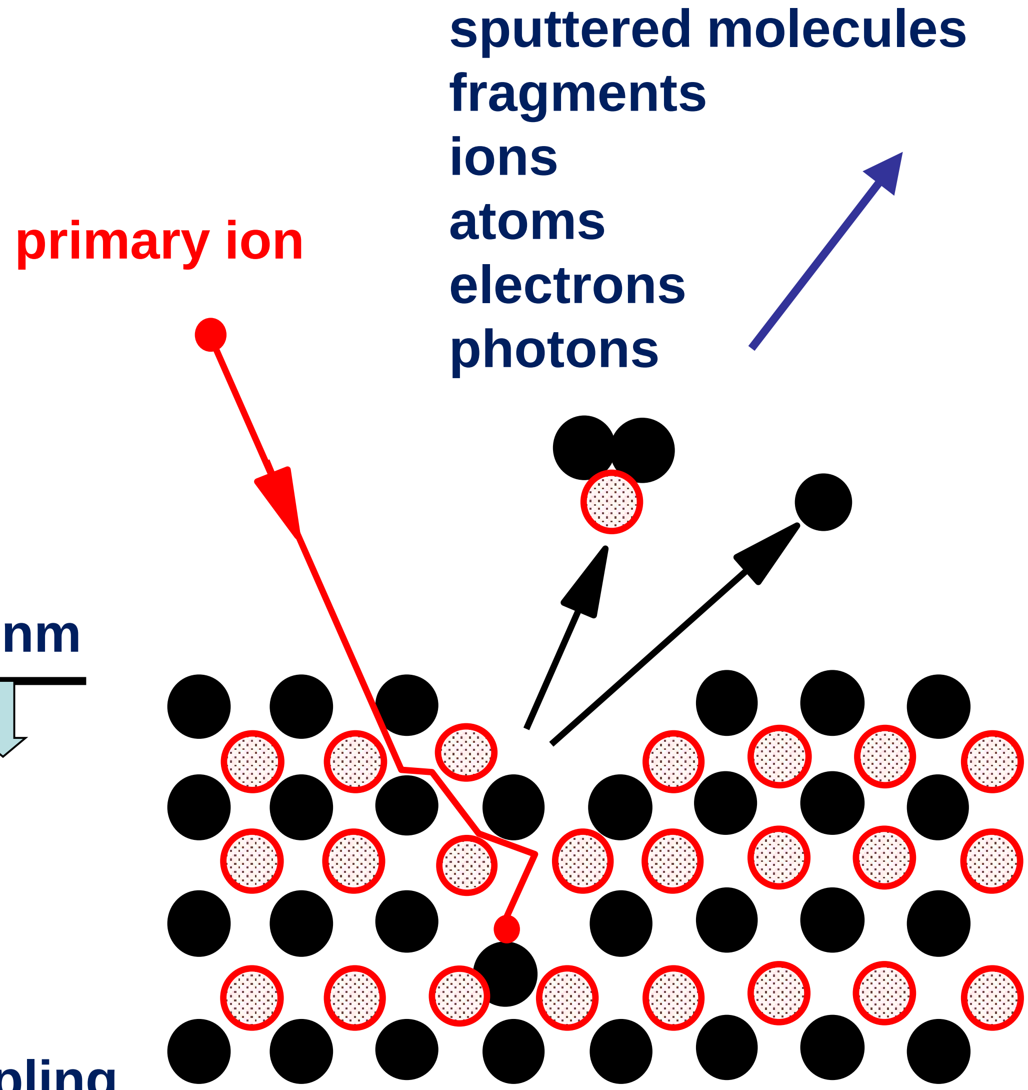
SSIMS

Static Secondary Ion Mass Spectrometry



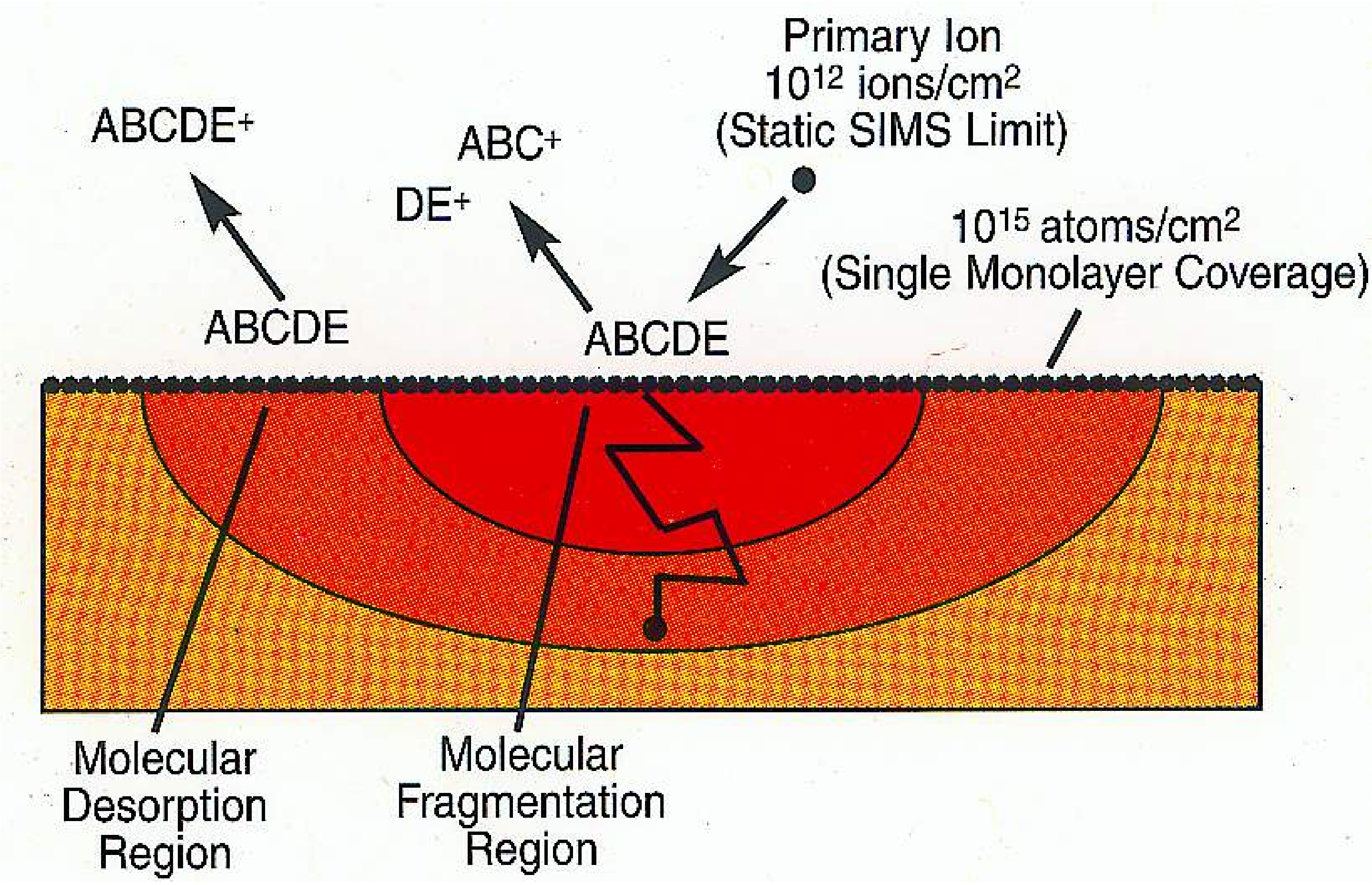
SSIMS


10nm
8nm
1-2nm
mixing
implantation
sampling


sputtered molecules
fragments
ions
atoms
electrons
photons
primary ion

SSIMS

Static Secondary Ion Mass Spectrometry



SSIMS

Static Secondary Ion Mass Spectrometry

Any type of mass spectrometer can be used:

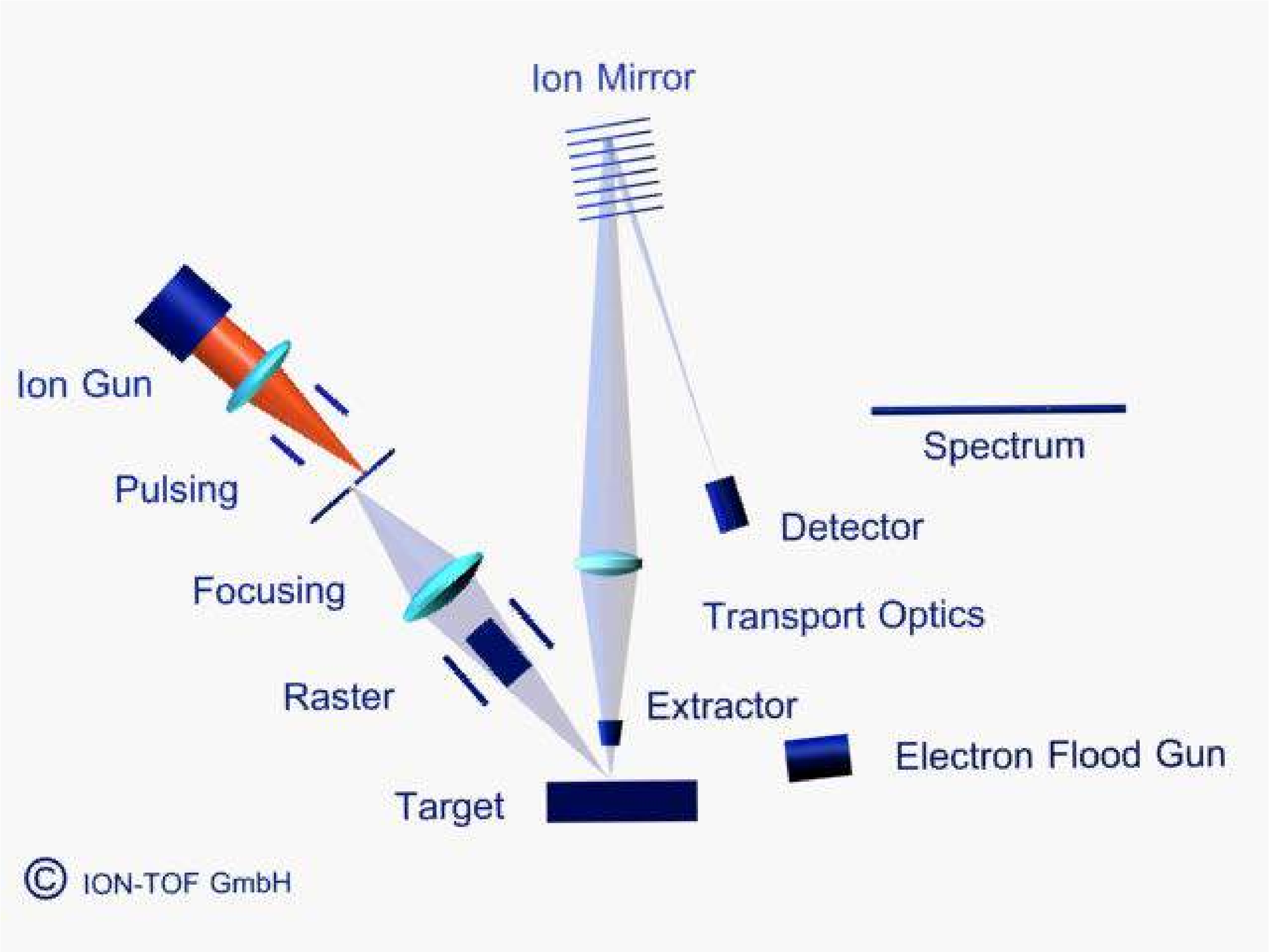
Quadrupole

Magnetic sector

Time-of-Flight $\Rightarrow$ **'ToFSIMS'**

- high transmission = high signal levels
- parallel detection = fast acquisition
- high mass resolution
- pulsed system

TOFSIMS



www.iontof.com

Surface Chemical Analysis by XPS and SIMS

The Ion-Tof 'ToF-SIMS IV – 200' Instrument

- 8" sample capability
- automation
- -150°C to 600°C

- Ga^+, In^+, Au_n^+, Bi_n^+, SF_5^+ Cs^+, Ar^+ and O_2^+ ion sources
  - high signal levels for molecular species
  - imaging of molecular species at ~ 0.3μm resolution

Surface Chemical Analysis by XPS and SIMS

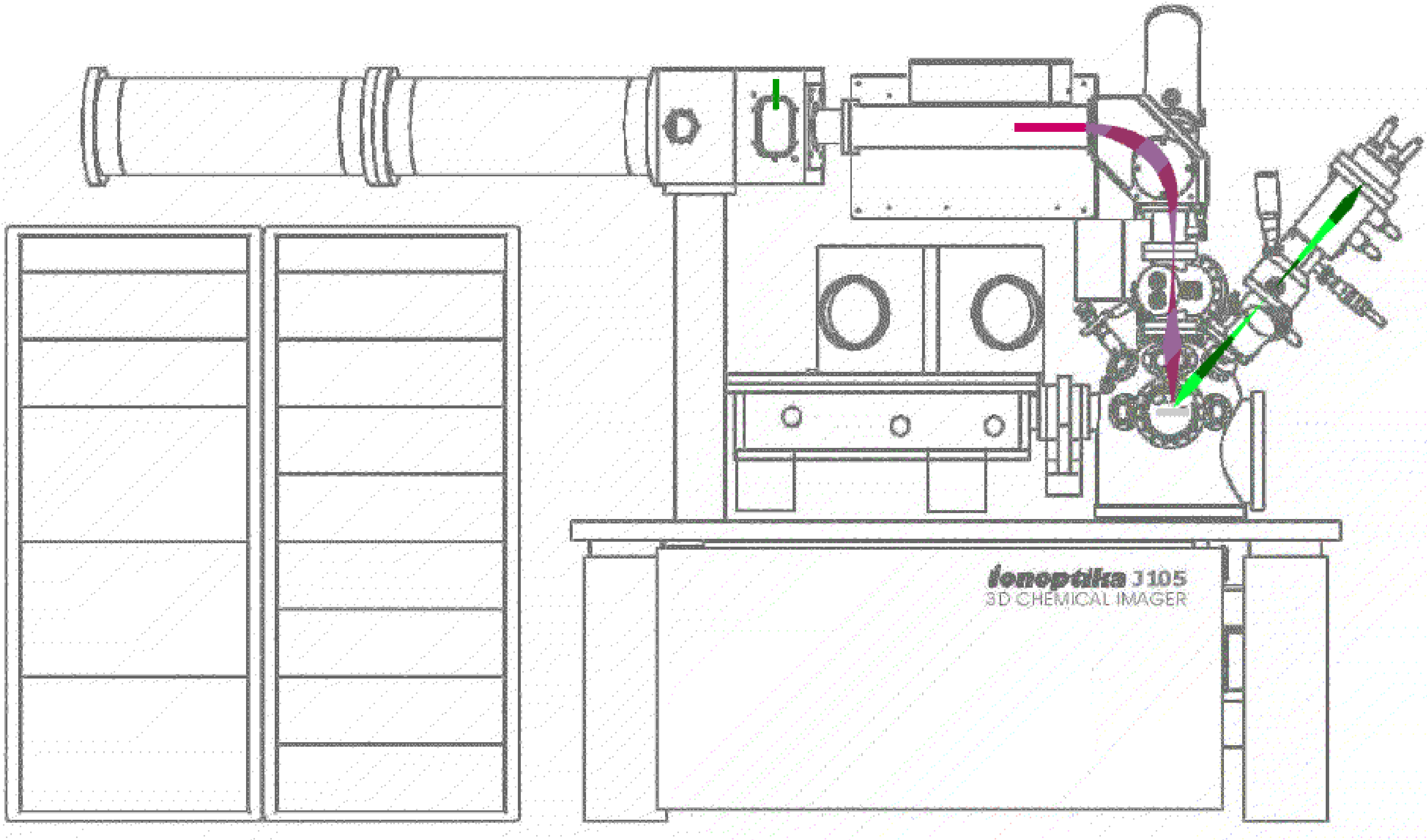
The Ionoptika J105 SIMS

Not only C_{60}^{+} and Ar_{4000}^{+} but also

$[H_2O]_{6000}^{+}$ cluster ion beam source ……

Surface Chemical Analysis by XPS and SIMS

Ionoptika J105 SIMS



What information is available?

- Detects all elements
- Mass range up to 20000 Da
- ppm - ppb sensitivity

- Spectrometry
  - ‘fingerprint’ characteristic spectra from Static SIMS
  - molecular identification of organic and inorganic species
  - *relative* quantification of molecular species
  - high mass resolution ($m/\Delta m$ ~10000+)

- Imaging
  - 0.3μm resolution

- Depth profiles
  - inorganic and organic materials
  - ~1nm depth resolution

Surface Chemical Analysis by XPS and SIMS

What information is available?

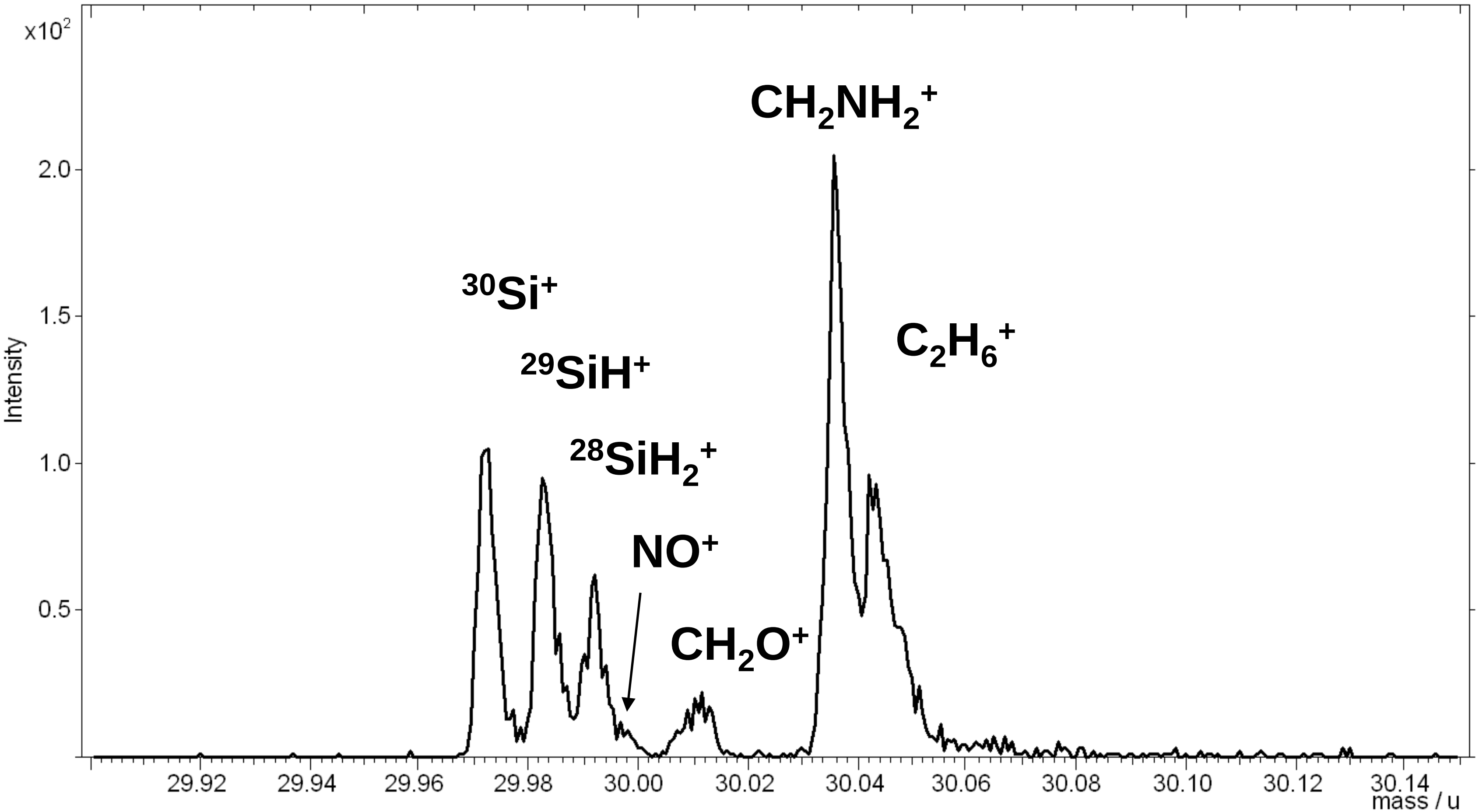
- ‘Retrospective’ spectrometry, imaging and depth profiling
  - Every 2D pixel or 3D voxel contains a full mass spectrum
- Solids and liquids
- Electrical conductors and insulators
- Analysis at -150°C up to 600°C
  - Thermal Desorption SIMS

High Mass-Resolution SSIMS

- $m/\Delta m$ = 10000+
- identify ion composition from accurate mass
- resolve inorganic from organic species (e.g. Fe^+ / $C_4H_8^+$)
- elemental and molecular information
- ppm sensitivity
- novel information
- facilitates relative quantification

- probe active surface chemistry
- identify poisons / deactivation mechanisms
- oxidation state information
- compound identification

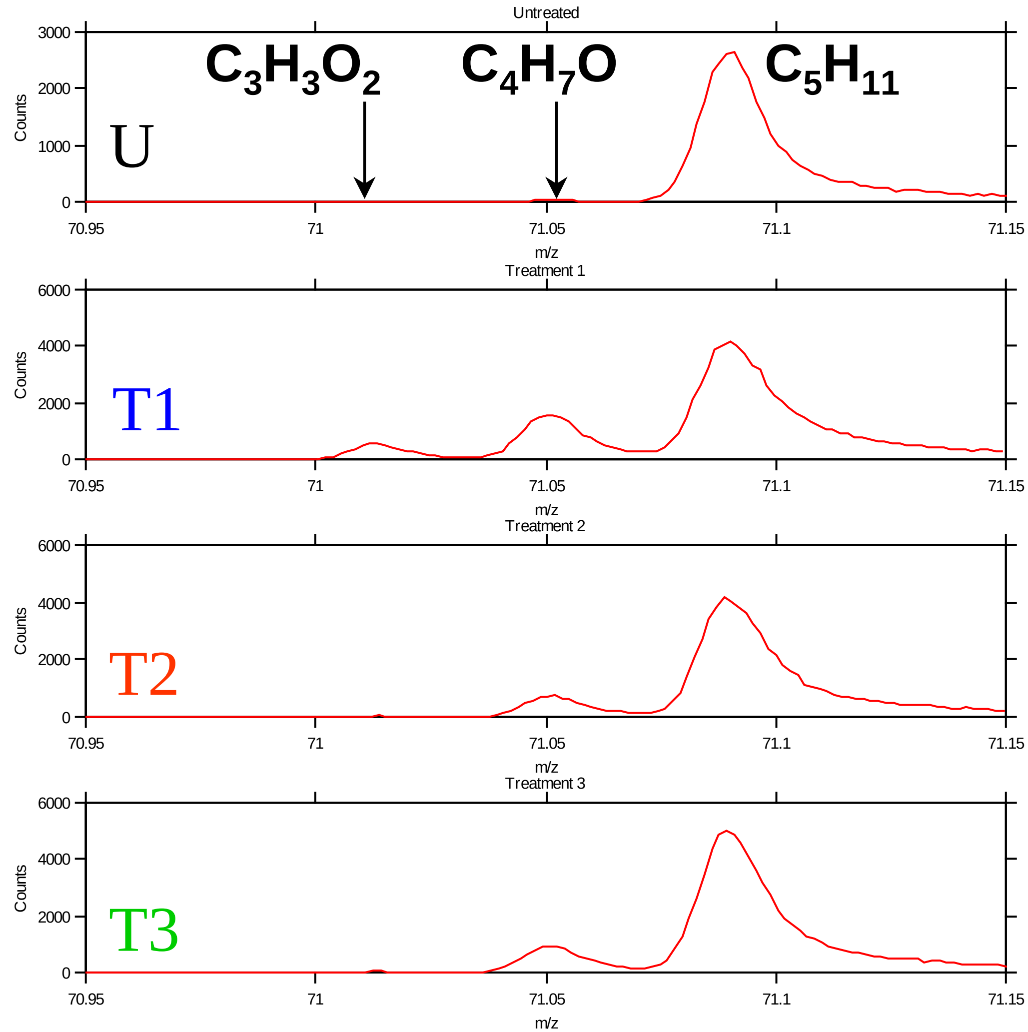
Si wafer m/z 30



Surface Chemical Analysis by XPS and SIMS

Positive ion high mass resolution SSIMS spectra

m/z +71

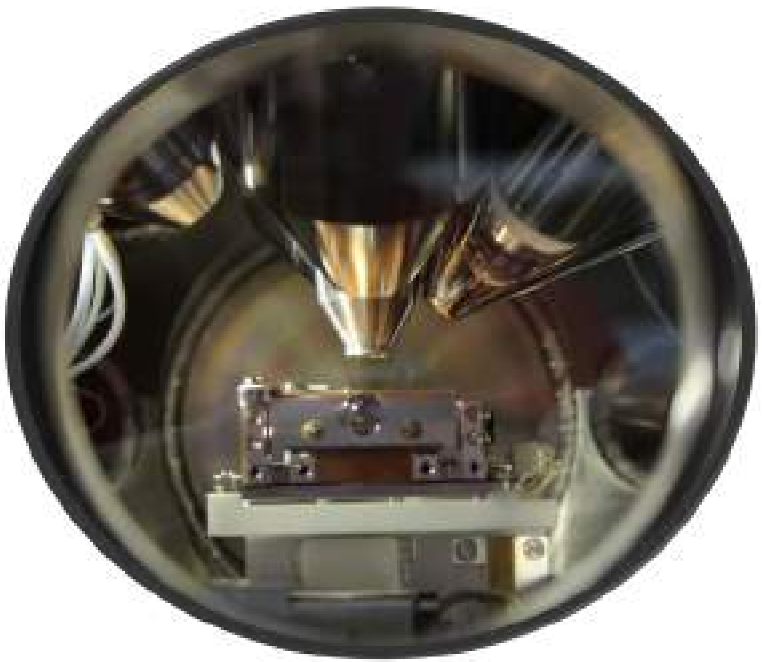


Discrete peak areas

Relative quantification

Latest developments …..

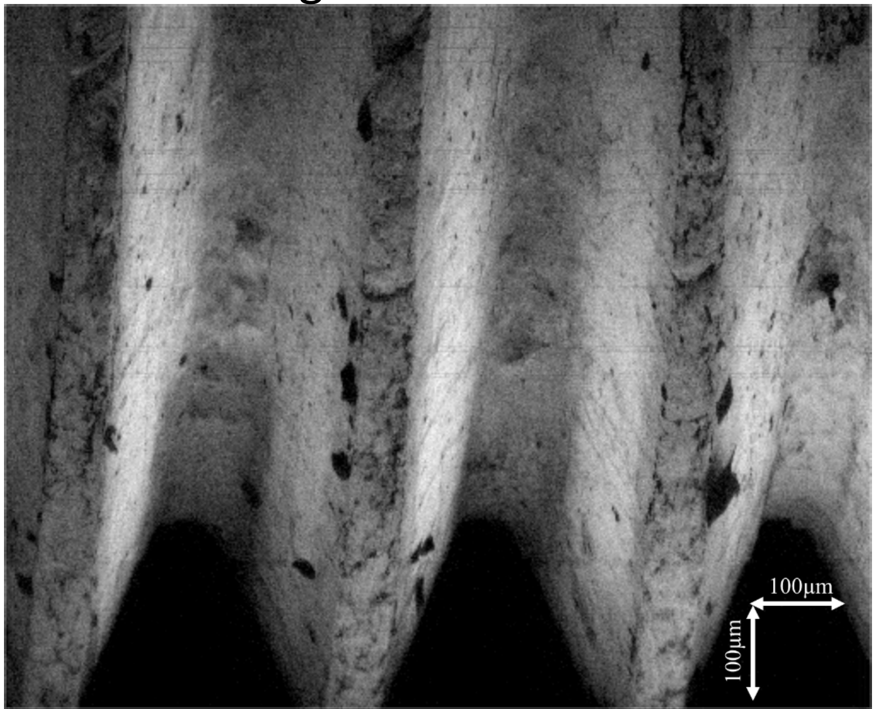
- Topography independent mass resolution



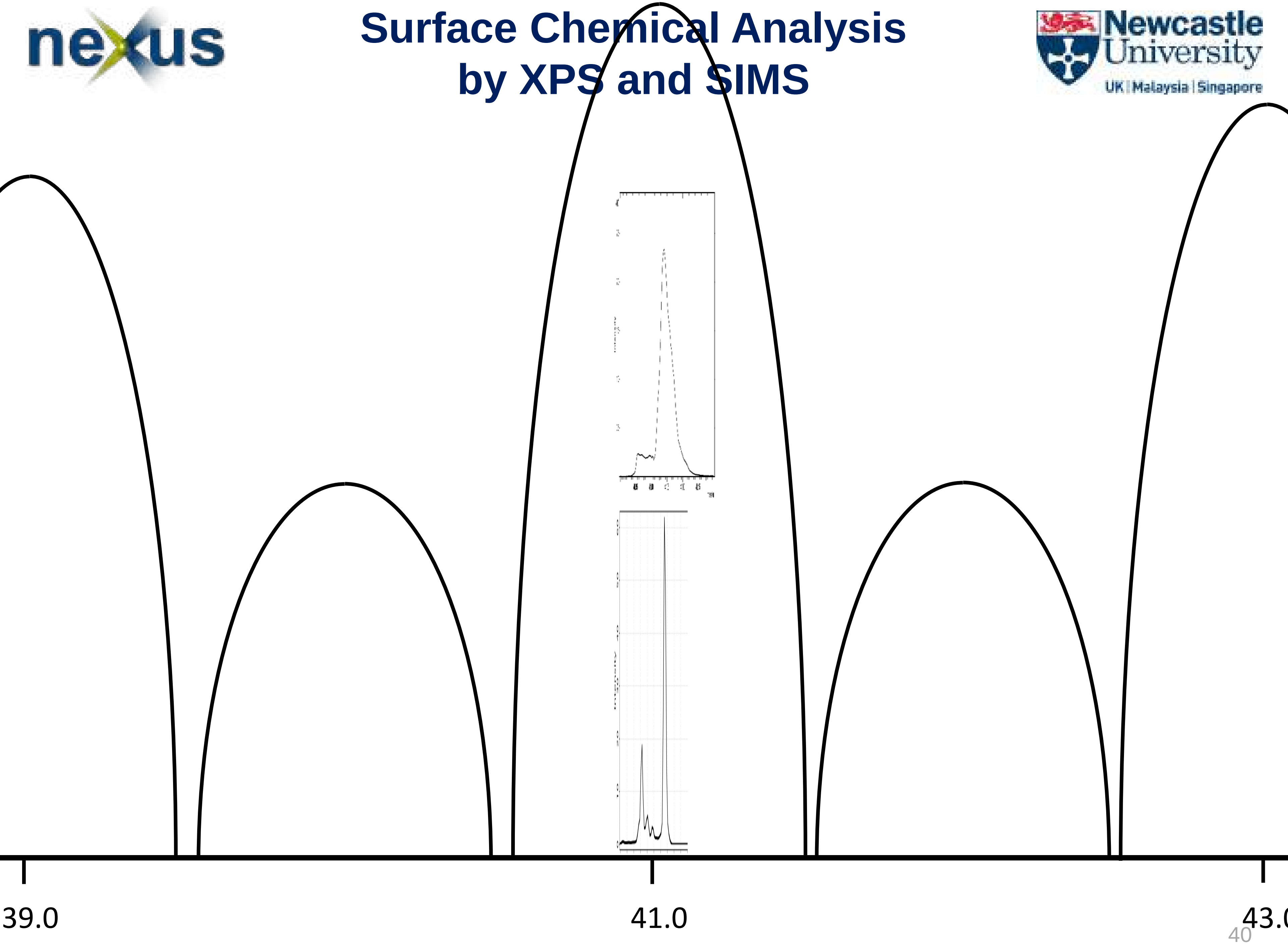
IONOPTIKA
ion beam technology

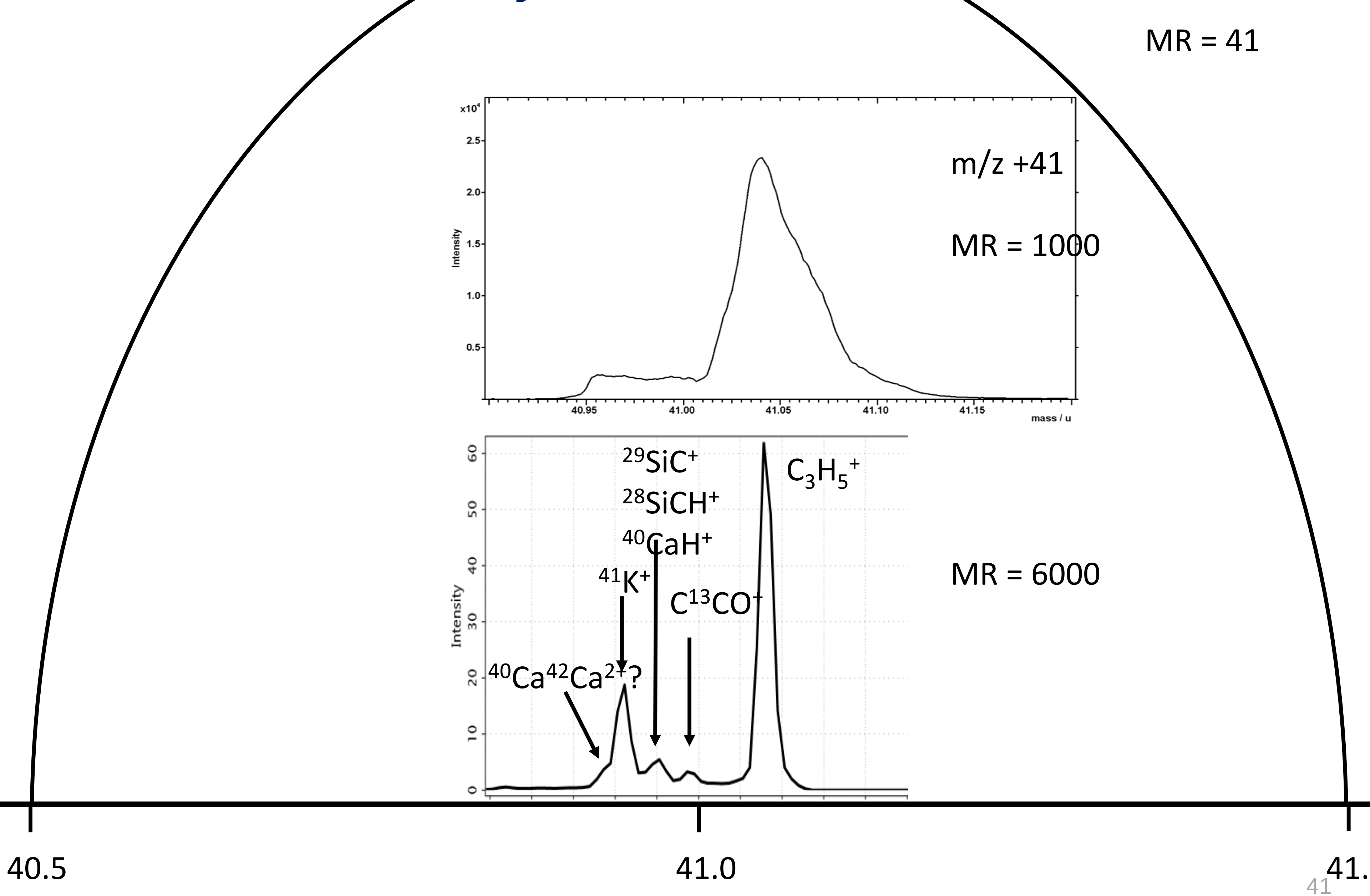
also Large Depth of Field

Cr image of an M1.6 screw



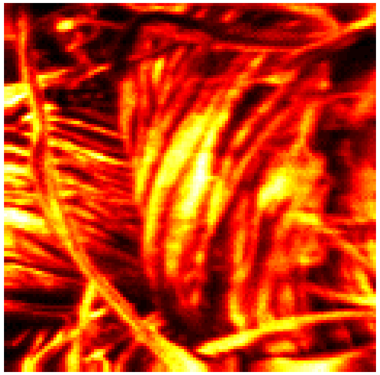
Surface Chemical Analysis by XPS and SIMS



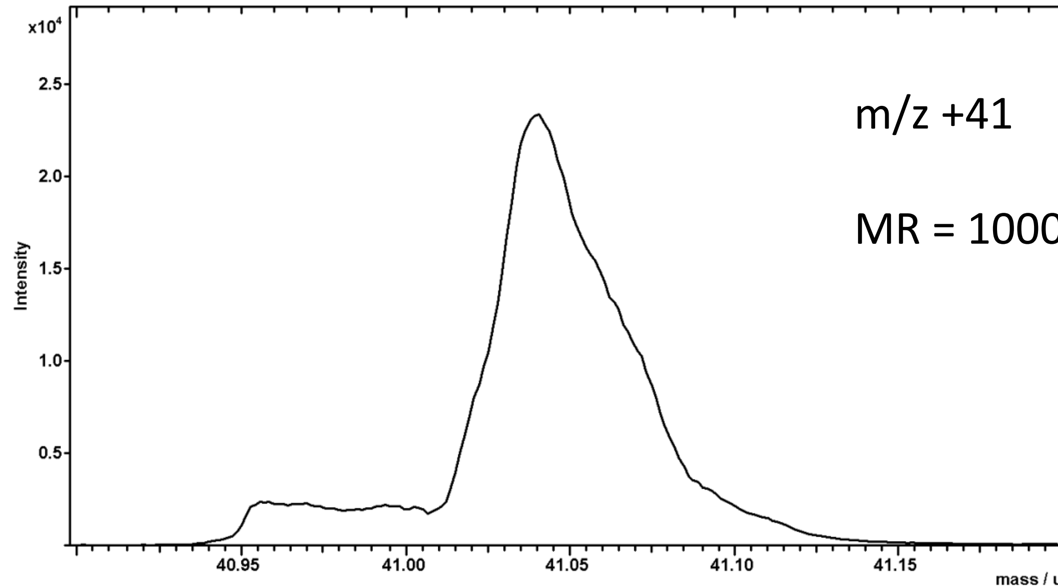

MR = 41
m/z +41
MR = 1000
MR = 6000
x10⁴
Intensity
mass / u
40.95
41.00
41.05
41.10
41.15
$^{29}SiC^+$
$^{28}SiCH^+$
$^{40}CaH^+$
$^{41}K^+$
$C^{13}CO^+$
$C_3H_5^+$
$^{40}Ca^{42}Ca^{2+}$?
40.5
41.0
41.

Surface Chemical Analysis by XPS and SIMS

'Traditional' design (Iontof, PHI):

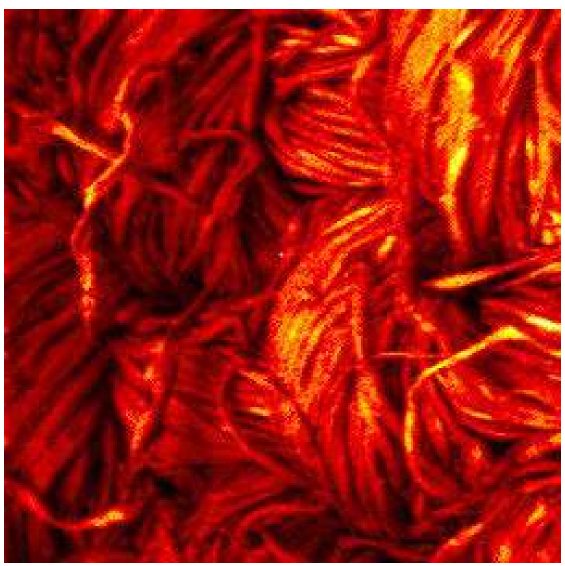


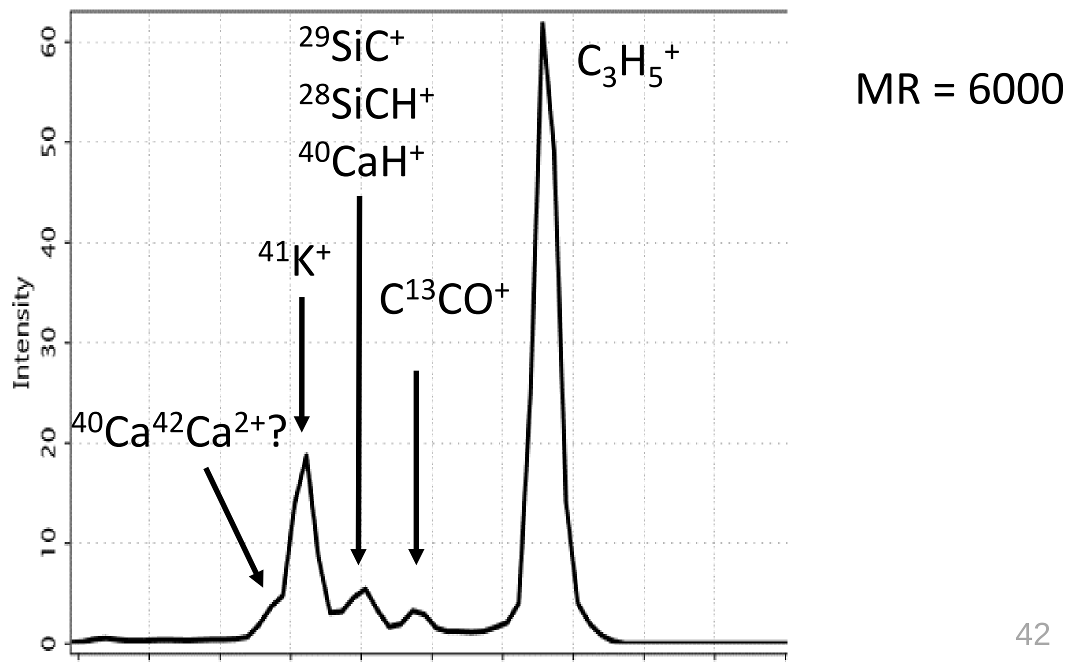
500µm x 500µm



J105:

750µm x 750µm





Imaging SSIMS

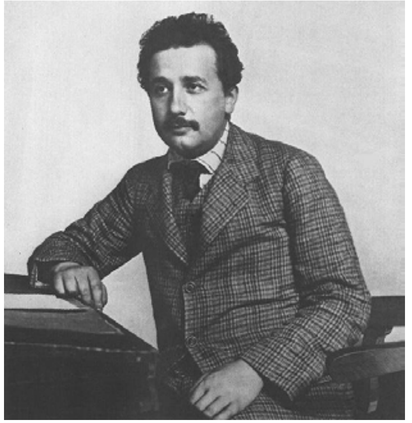
Molecular species, elements, small fragment ions
ca. 300nm spatial resolution
'Hyperspectral' Imaging - every pixel contains a full mass spectrum

Science:

distribution / location of species
structure / property relationships
migration studies
coating defects / small area analysis

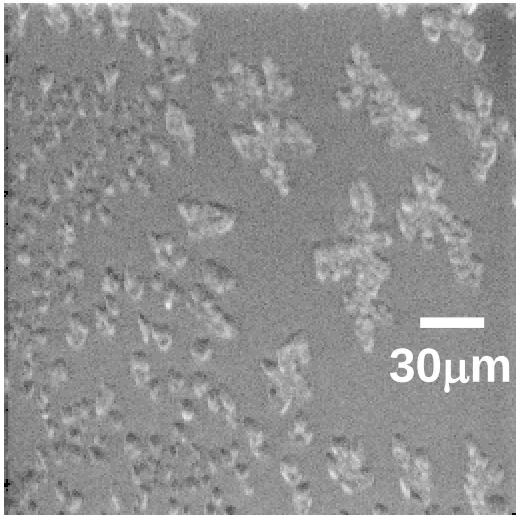
Sales and Marketing:

getting the message across
"If I can't picture it, I can't understand it"

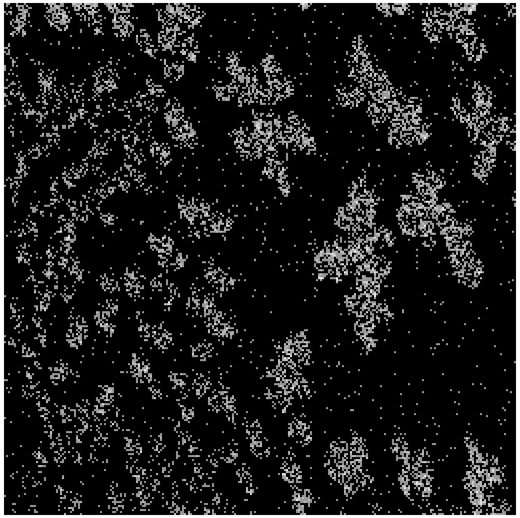


Segregation of PET trimer

Heated PET film:



Total Ion Image



PET trimer
m/z +577

Surface Chemical Analysis by XPS and SIMS

Single 50μm particle on a 3.5” Floppy Disk surface

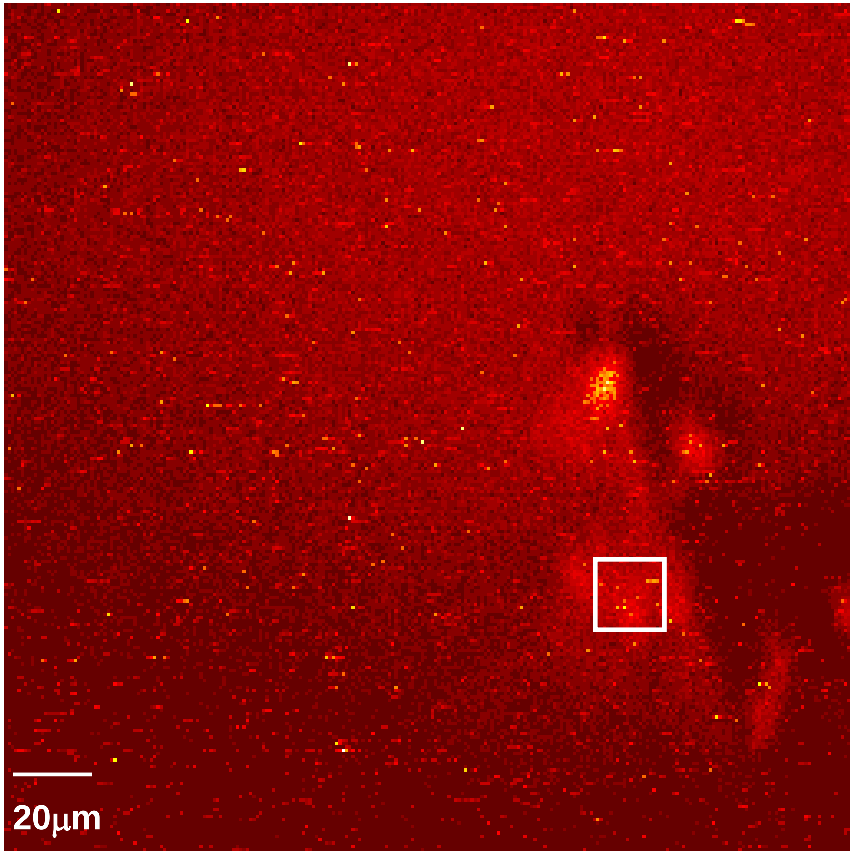
Imaging SSIMS analysis

- each pixel has a full mass spectrum
- select defined small areas
- regenerate spectra

PET particle on top of coating

- clean up
- modify machinery

- 100% pass rate for particulates!
- reduced costs



Surface Chemical Analysis by XPS and SIMS

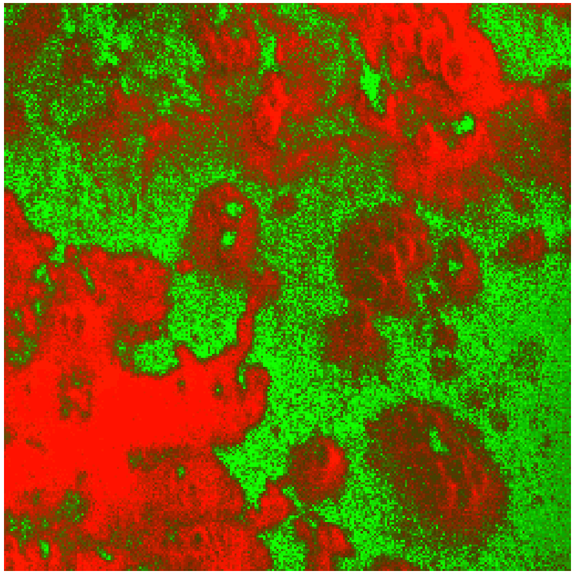
Coating problem

unexpected segregation of 2 coating components identified by SSIMS

product not working at all
6 months wasted project time

process modified
repeatable, uniform coverage

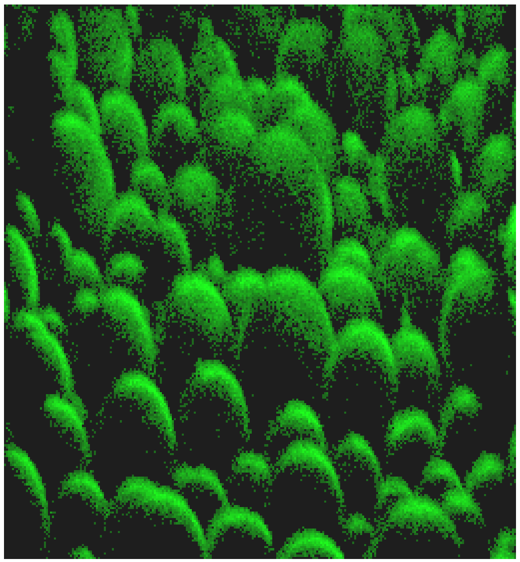
product working as predicted!



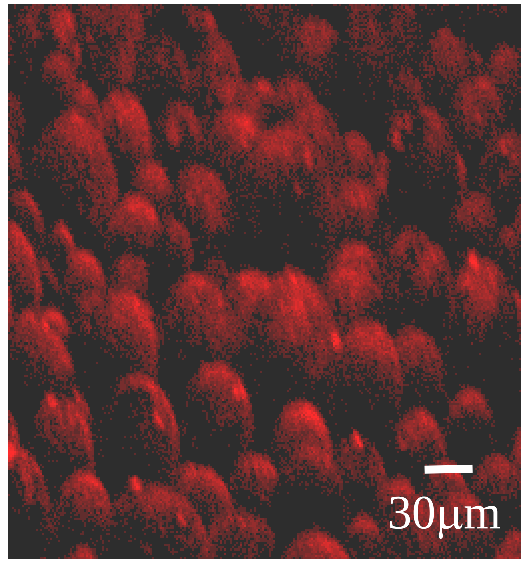
250µm x 250µm

Surface Chemical Analysis by XPS and SIMS

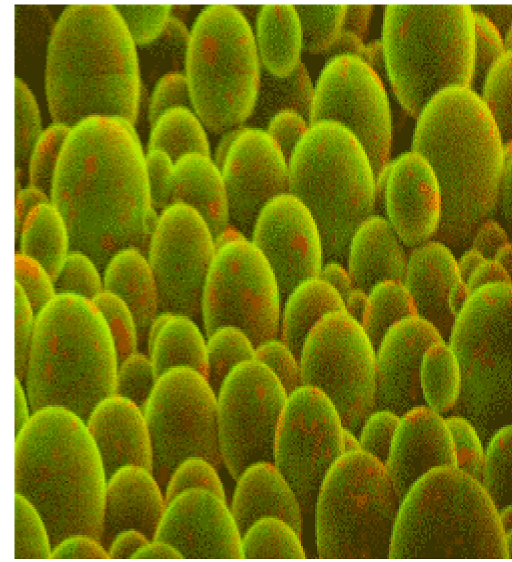
SSIMS Images of coated polymer microspheres



Surfactant



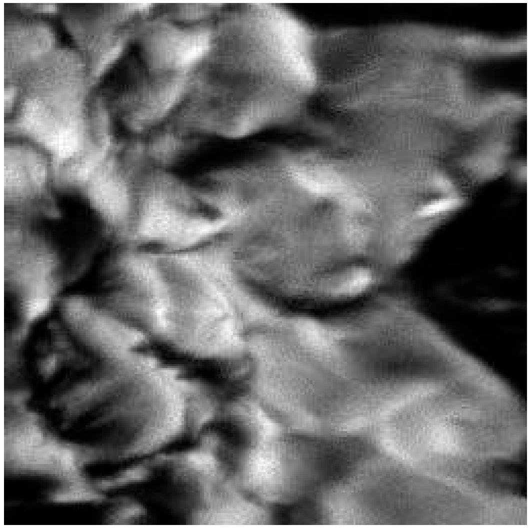
Contaminant



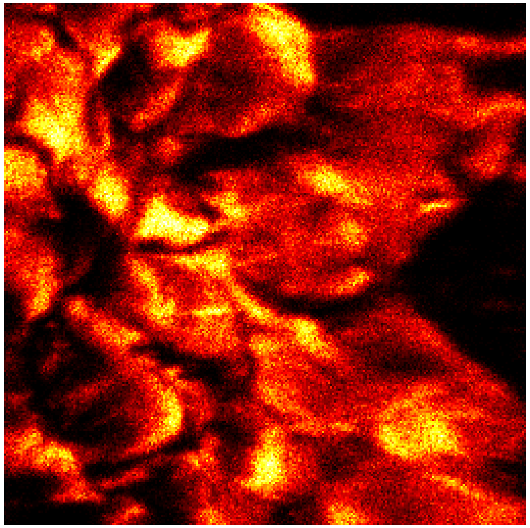
Surfactant (green)
Contaminant (red)

XPS indicated the average surfactant thickness = 0.9nm

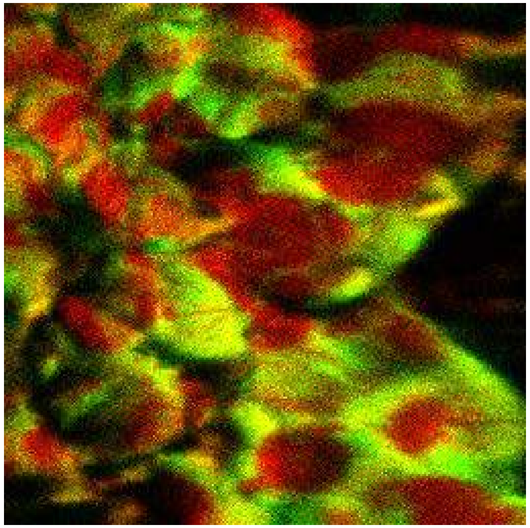
Static ToFSIMS images of a flavoured potato crisp:



Total Ion Image



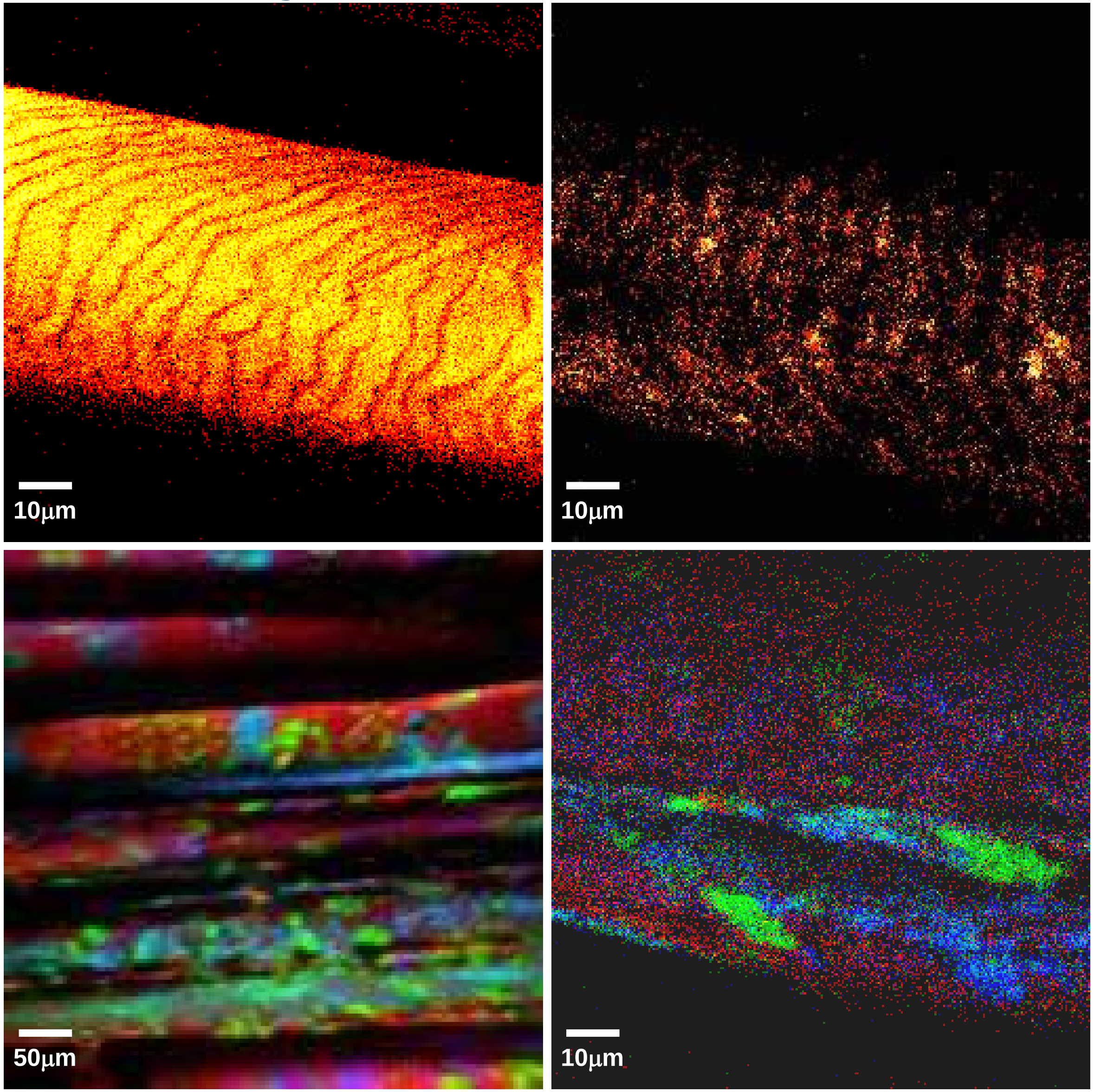
Diglycerides



Na (green)
Flavour Enhancer (red)

500μm x 500μm

Surface Chemical Analysis by XPS and SIMS



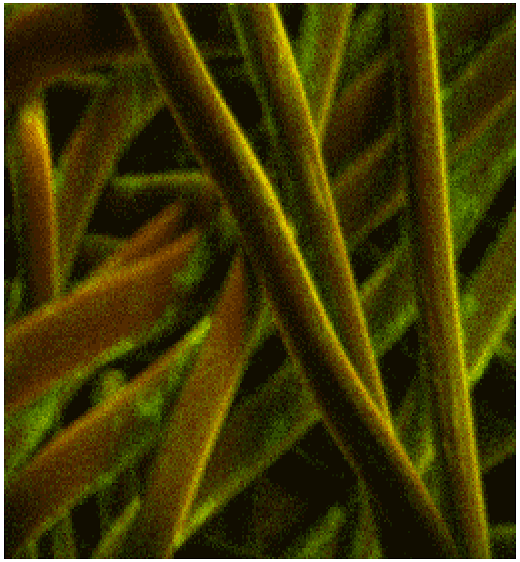
Molecular SSIMS images from human hair showing various treatment residues

SSIMS Images of Polypropylene fibres used in nappies

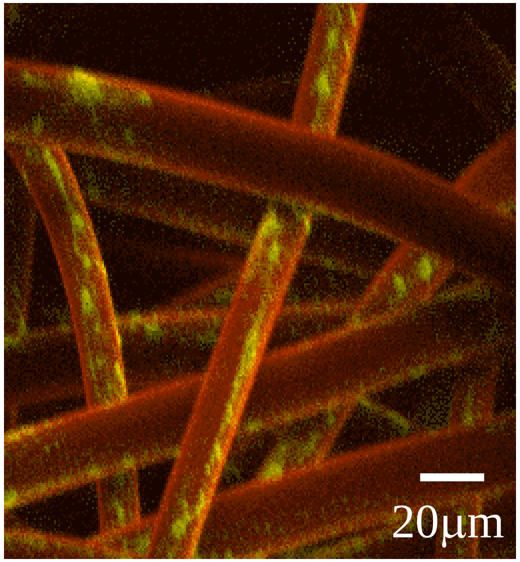
Product Performance depends on:

- Fibre surface chemistry / treatment
- Surface coverage
- Porosity of the non-woven fabric

- ‘ESC’ treatment more uniformly distributed
- ‘ESC’ treated fabric outperforms competitive materials



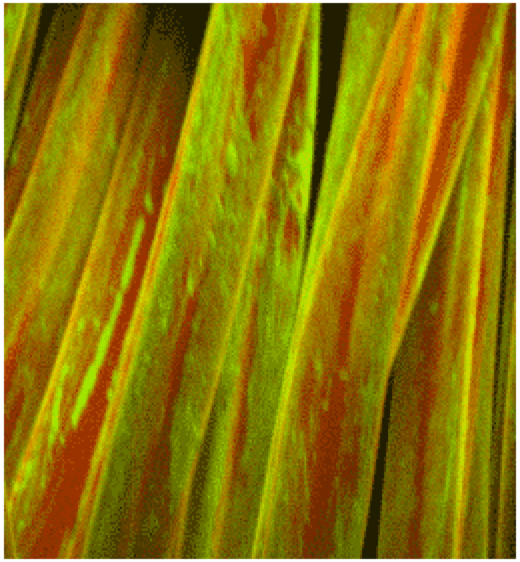
ESC



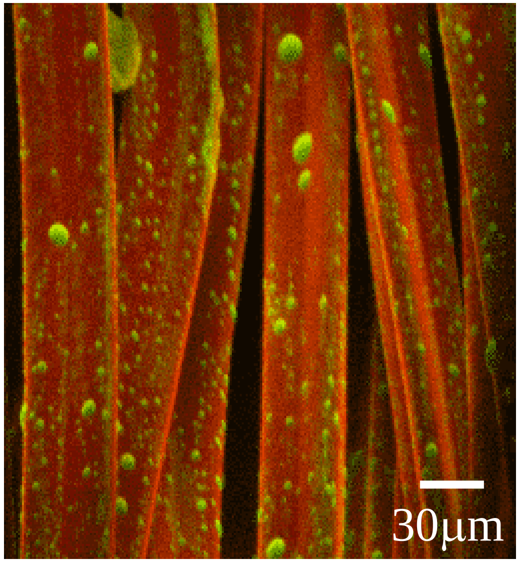
Competitor

SSIMS Images of Polypropylene carpet fibres

- Tri-lobal fibres
- Treatment to reduce friction during processing
- ‘ESC’ treatment applied at 5x lower level
- Outperformed competitive treatments
- Images used for Sales & Marketing



ESC



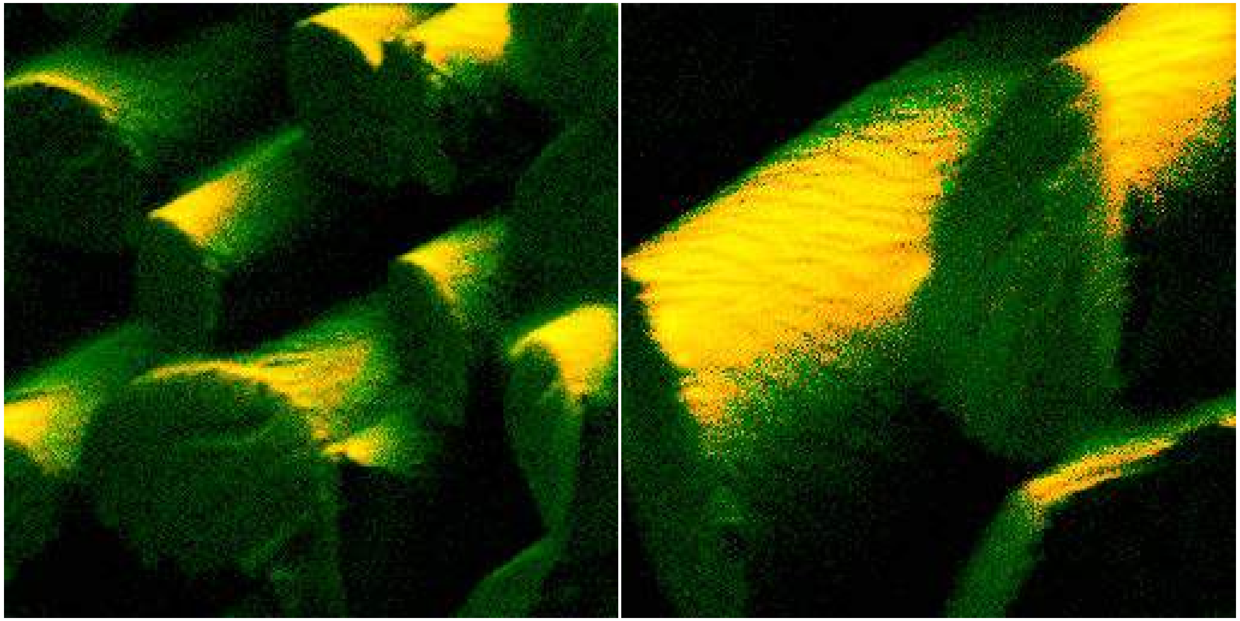
Competitor

“A picture paints a thousand words…”

Detection of Volatile Materials

Fragrances on Human hair:

- small molecules, volatile / mobile species: analysis at -110 °C
- treatment shown in ‘yellow / red’, $[M-H]^-$



250µm x 250µm   128µm x 128µm

Secondary Ion Mass Spectrometry – 'SIMS'

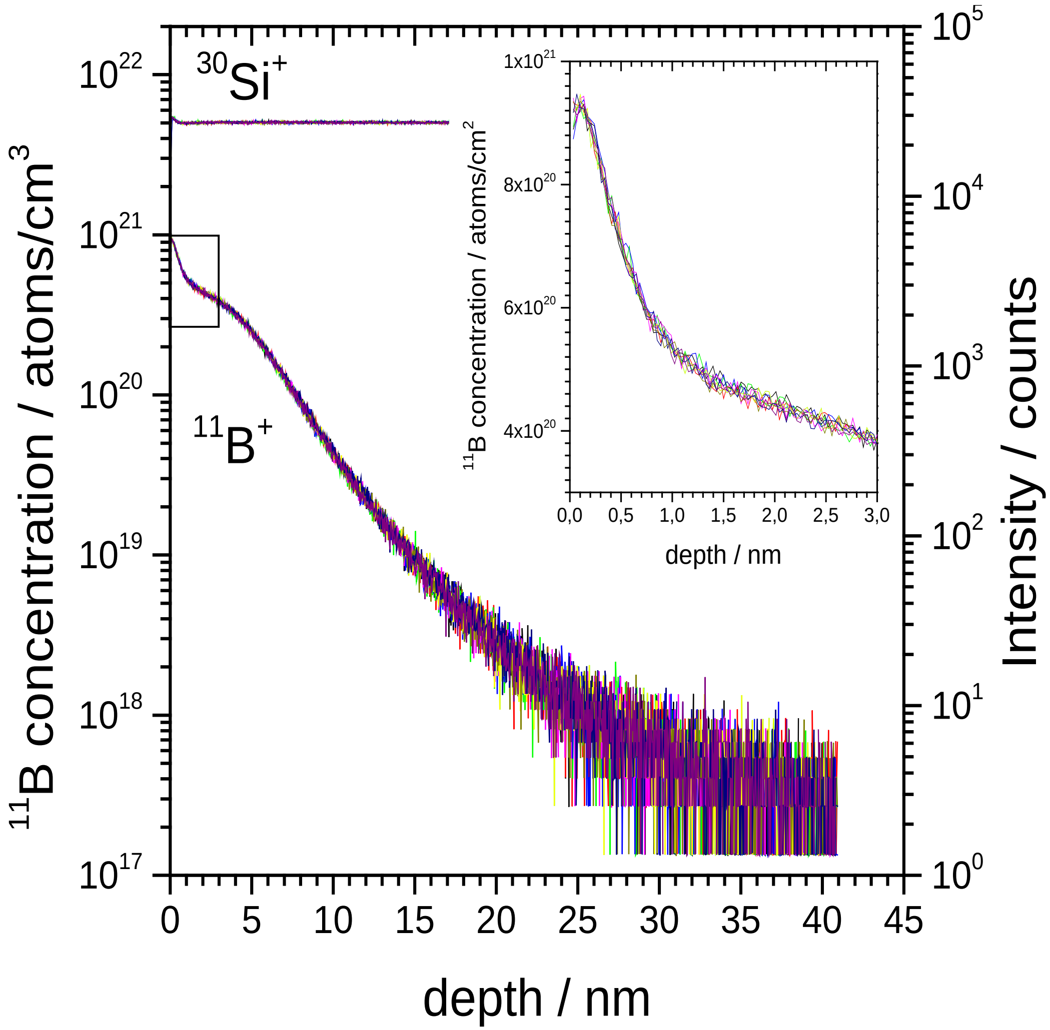
'Static' mode	'Dynamic' mode
SSIMS	DSIMS
Low sample damage	High sample 'damage'
'Fingerprint' spectra	Composition depth profiles

Primary Ion Dose Density

<1×10^{12} ions cm^{-2} >1×10^{13} ions cm^{-2}

Typical surface = 1×10^{15} atoms cm^{-2}

Depth Profiling – Dynamic SIMS

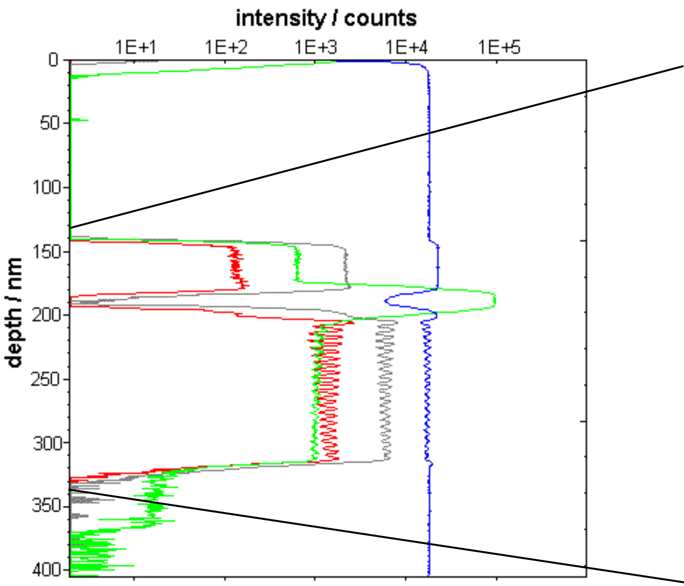


Sample:

700 eV B^+ implant in Silicon

Surface Chemical Analysis by XPS and SIMS

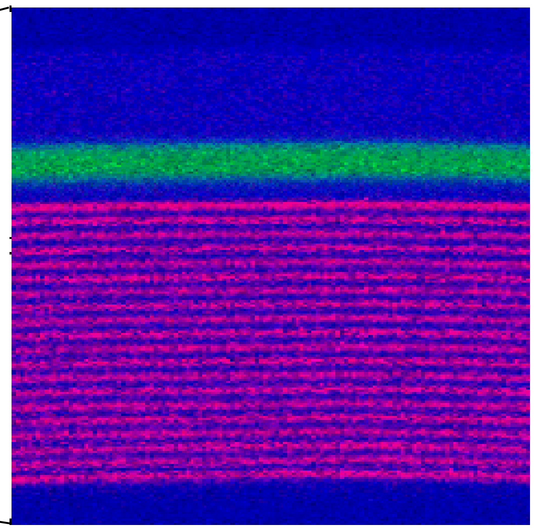
Depth Profile



red: Al_2
green: In
grey: GaAl
blue: Ga_2

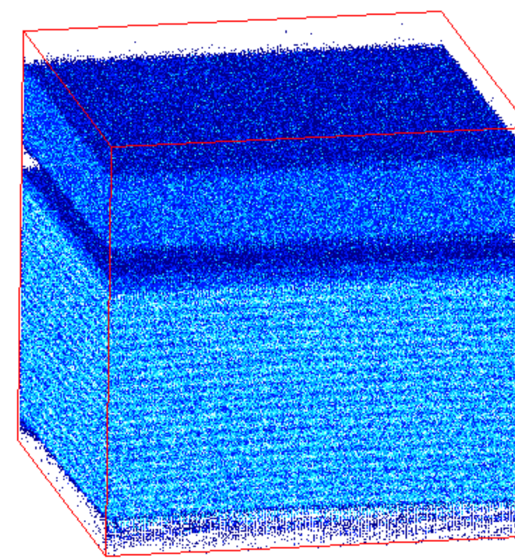
2D Cross Section

Field of View: 60 x 60 µm^2



Overlay Image
red: Al_2
green: In
blue: Ga_2

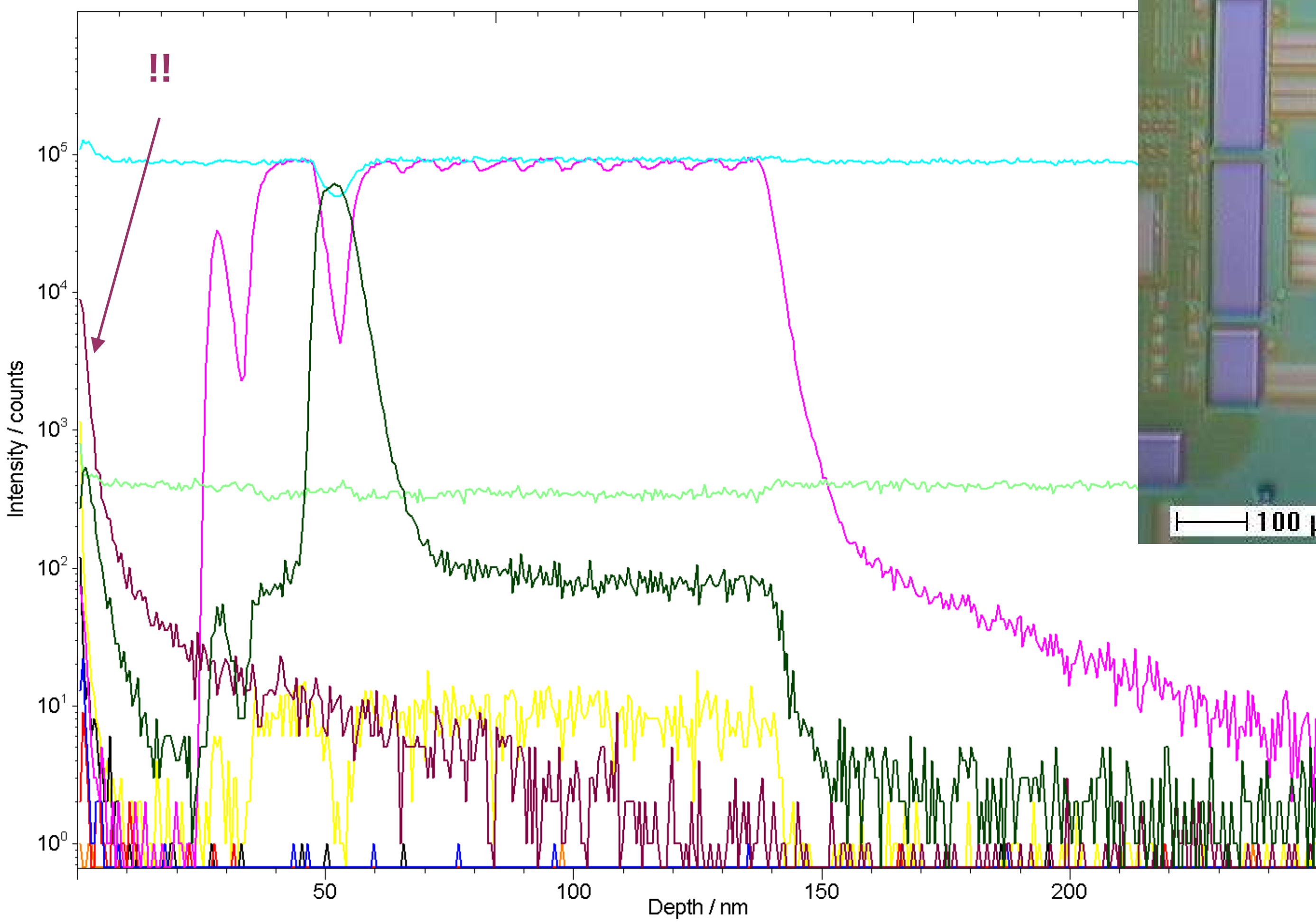
3D Render

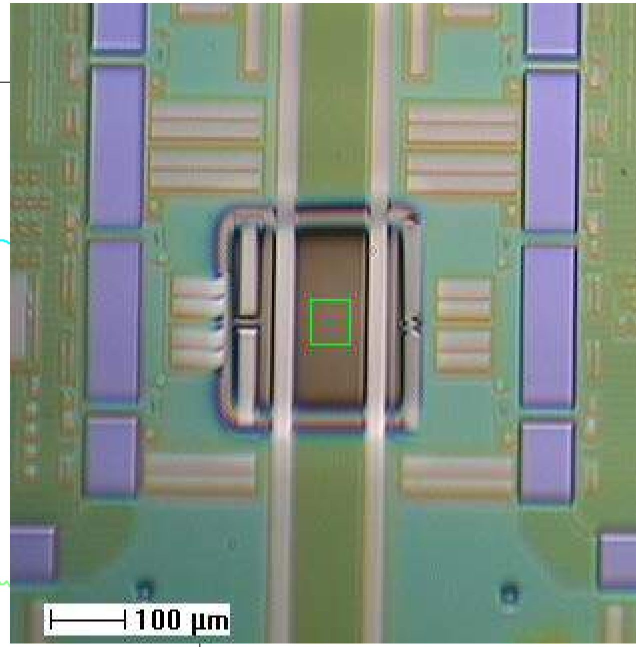


3D Distribution
example: Al_2+GaAl

Surface Chemical Analysis by XPS and SIMS

Depth Profiling – Dynamic SIMS





Typical Questions Asked:

Specific:

- Is there any X present?
- How much is present?
- How is it distributed?
  - 1- or 2-D
  - depth
  - 3-D
- Locus of failure?

General:

- What is it?
- Where is it?
- What is different between good and bad samples?
- Why is it failing?
- Why won't it stick?
  - adhesion
  - laminates
  - printing / coating
- Why is theirs better than ours?

R&T, Production, Process monitoring / development, QC, Patent protection, SHE

Typical applications:

- failure analysis – laminates, metallised layers, heat-seal adhesive joints, coating issues
- coating defects
- printing defects
- adhesive developments
- materials developments
- surface pre-treatment
- primer developments
- contamination
- corrosion studies
- additive migration / bloom
- competitive material analysis
- pharmaceutical / medical
- ….

Surface Chemical Analysis by XPS and SIMS

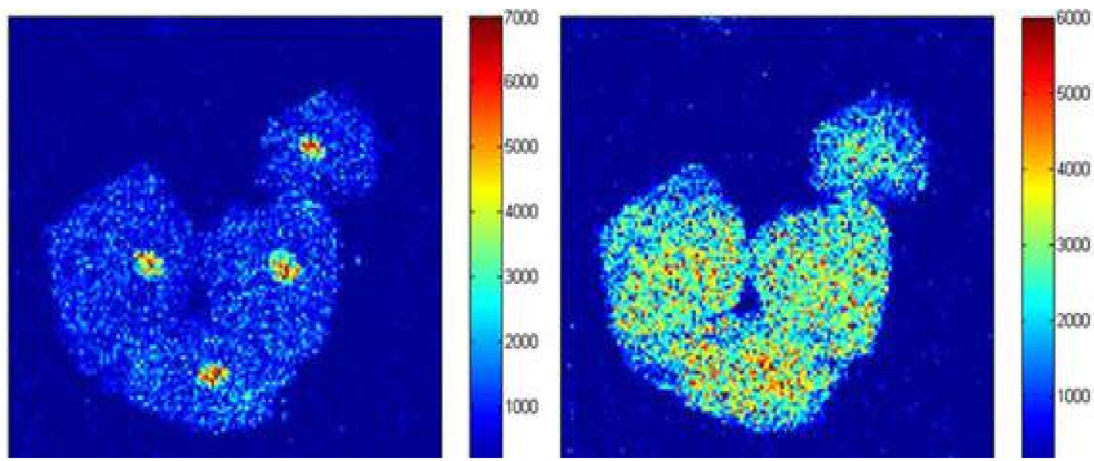
Latest developments …..

- Topography independent mass resolution
- C_{60}^{+} ion source
- Ar_{4000}^{+} cluster ion source
- $(H_2O)_{6000}^{+}$ cluster ion source
- Mass Spec – Mass Spec MSMS
- 10nm spatial resolution
- SALVI

Surface Chemical Analysis by XPS and SIMS

Latest developments …..

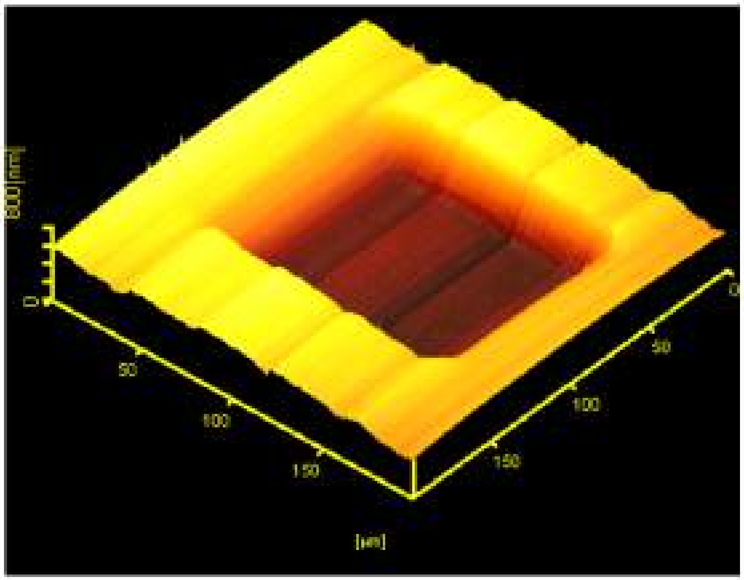
- C_{60}^{+} ion source
  - 200nm spatial resolution
  - enhanced signal levels for molecular species
  - organic, inorganic and mixed depth profiling
  - analysis of buried interfaces

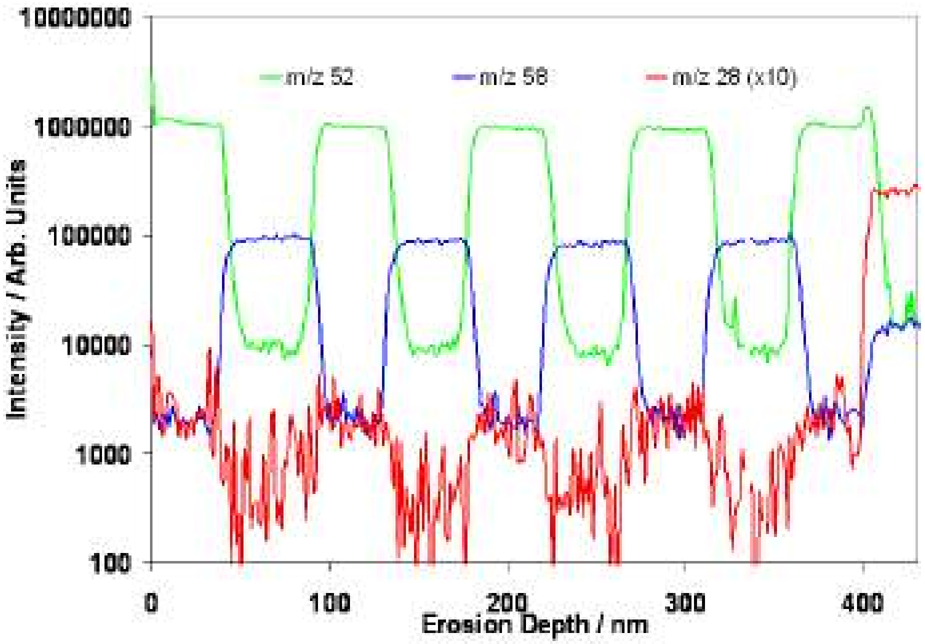


IONOPTIKA
ion beam technology

Depth Profiling – Dynamic SIMS

NIST NiCr sample, 66 and 53 nm alternating layers. C_{60}^{+} ion source





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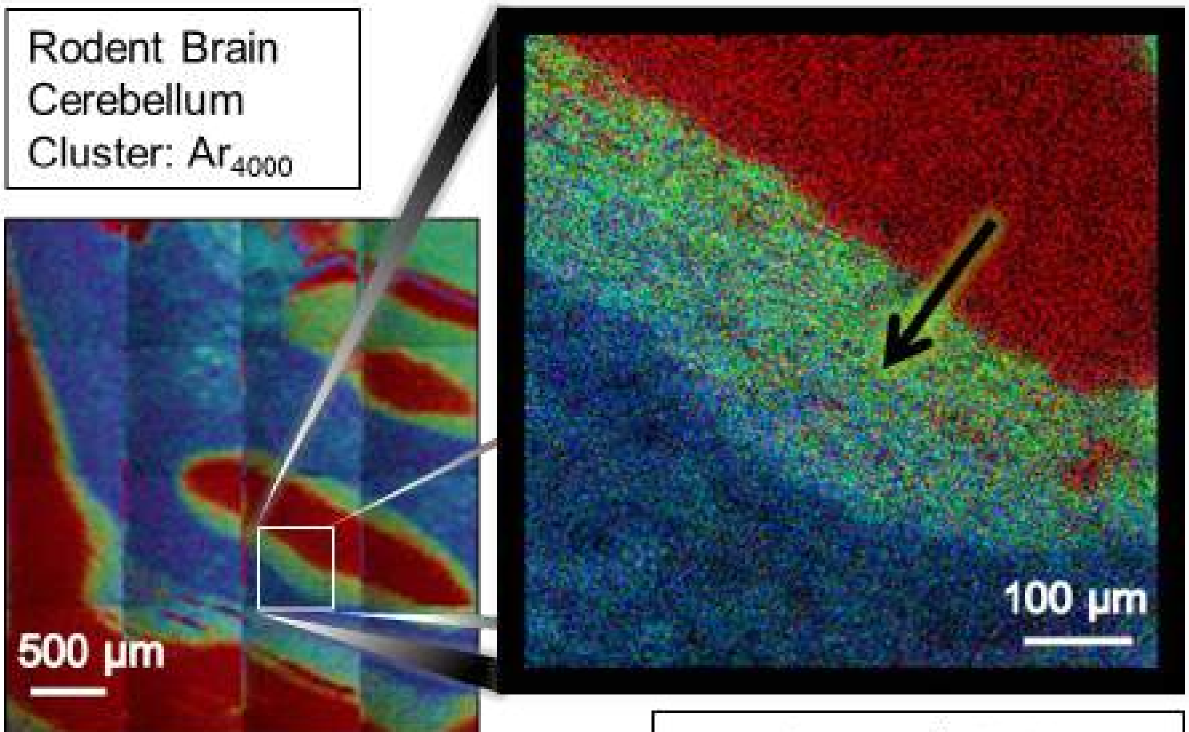
ion beam technology

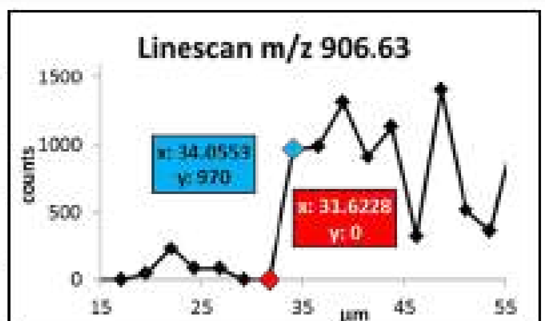
Latest developments …..

- Ar_{4000}^{+} cluster ion source
  - 500, 1000, 2000 and 4000 cluster sizes
  - 2 micron spatial resolution
  - analysis of real (contaminated) samples
  - enhanced signal levels for molecular species
  - organic depth profiling
  - analysis of buried interfaces

Surface Chemical Analysis by XPS and SIMS



m/z	Δppm	Label	Formula
890.6385	-0.64	C24 Sulf	$C_{48}H_{92}SNO_{11}$
906.6328	-1.31	C24-OH Sulf.	$C_{48}H_{92}SNO_{12}$
885.5509	1.83	PI(38:4)	$C_{47}H_{82}O_{13}P$



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ion beam technology

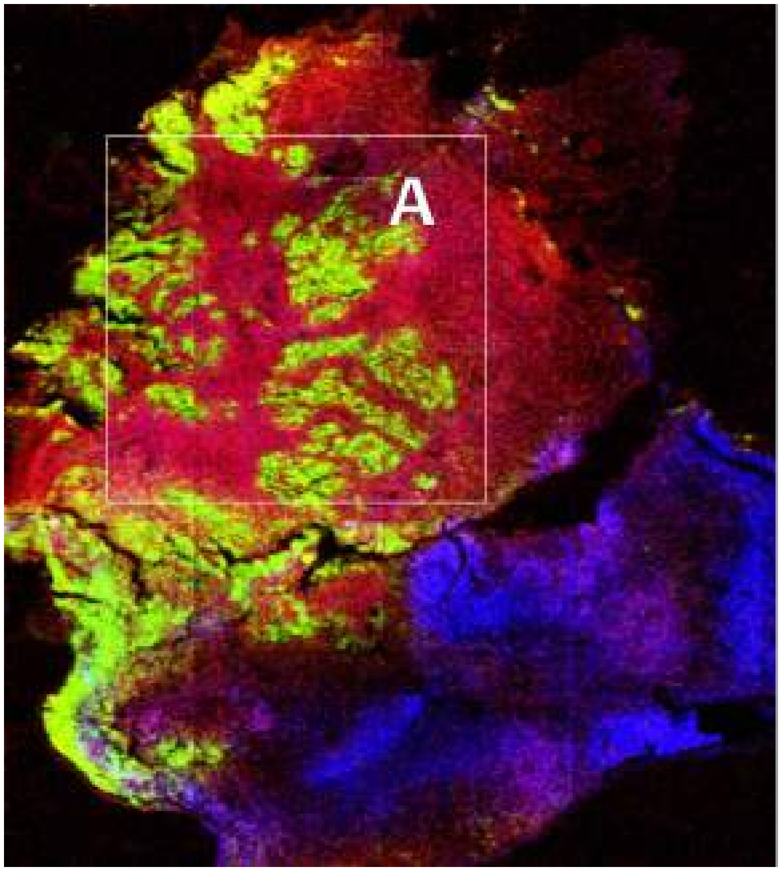
Imaging intact lipid species in mouse brain tissue.

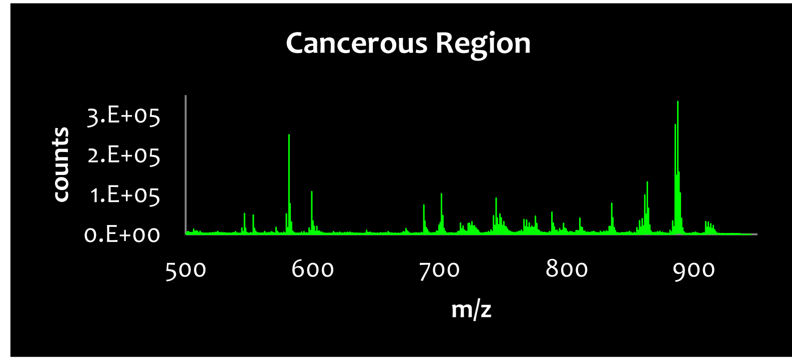
Large Image is 2.5 × 2.5 mm^2, 10 µm/pixel

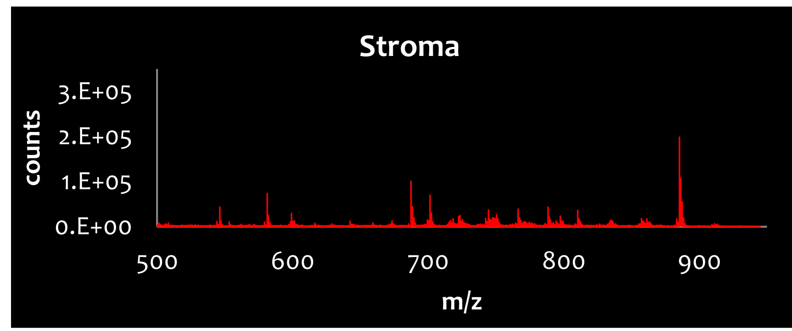
Detailed image has area 512 x 512 mm^2 acquired at 2 µm/pixel.

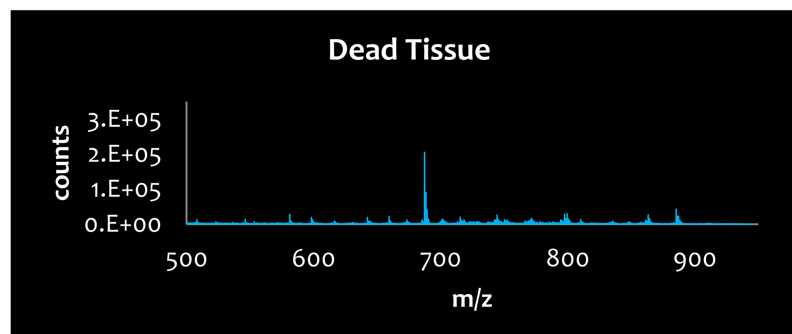
Dose of 6e12, negative ion mode

Freeze dried biopsy tissue







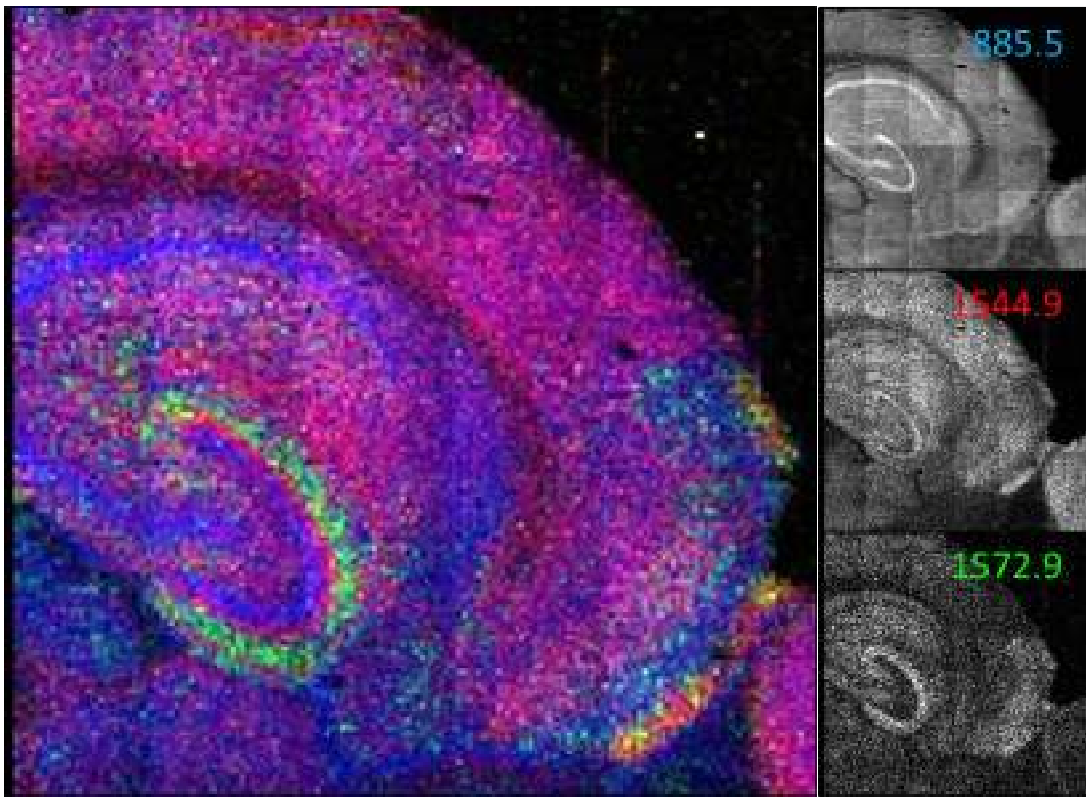


m/z 887.4 PI(38:3)
m/z 788.4 PS(36:1)
m/z 687.4 SM(33:1)

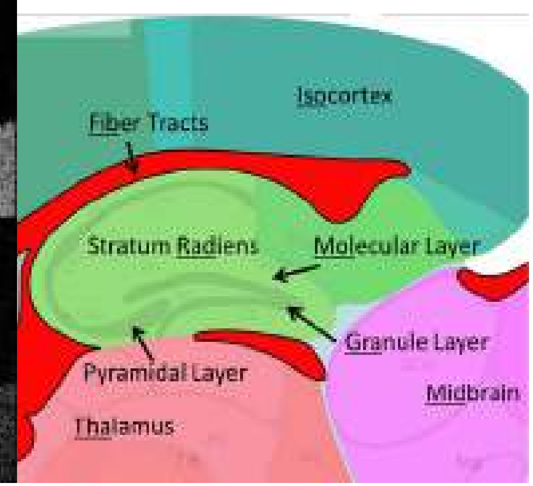
IONOPTIKA ion beam technology

Single peak mass images, full mass spectrum available at each pixel

Tissue Imaging with Ar_{4000} on frozen hydrated tissue section



All data was acquired using 40 keV Ar_{4000}^{+}, ion dose: 1×10^{12} ions/cm^2, negative ion mode. FOV is 5 mm.



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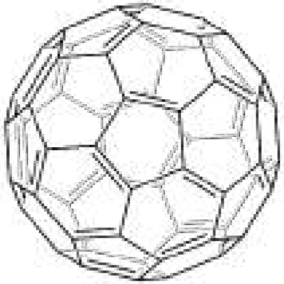
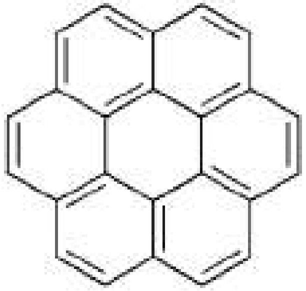
ion beam technology

Depth profiling of Organic Materials

SSIMS destroys the surface

- How to get more useful signal from the same amount of surface?
- Use cluster ion beams e.g. Au_x^{n+}, Bi_x^{n+}, Ar_{4000}^{+}
  or polyatomic ions SF_5^+, C_{60}^+, $C_{24}H_{12}^+$
  or low energy Cs^+ e.g. 200eV



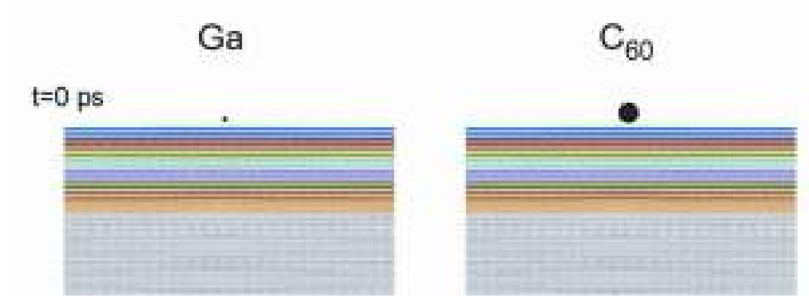


- Lower impact energy per atom
  - less mixing, fragmentation and sub-surface damage
- More signal from molecular species for a given ion dose
  e.g. Bi_3^{2+} ca. 50000 x Ga^+
- No apparent damage?

Surface Chemical Analysis by XPS and SIMS

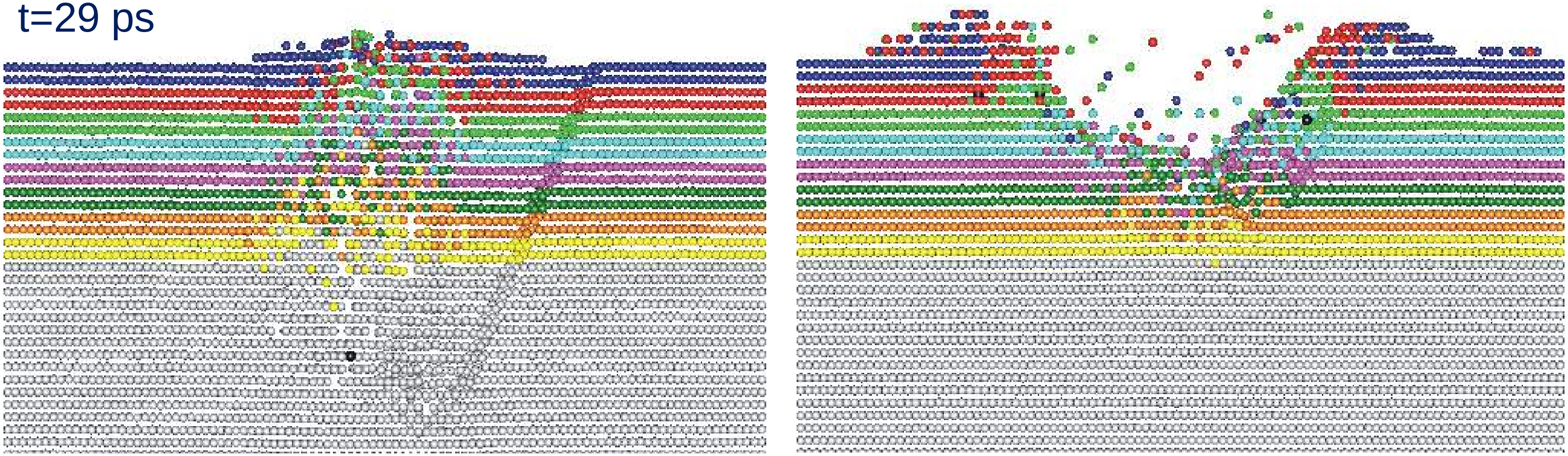
- **Larger volume is altered for Ga**
- **15x more material removed with C_{60}**

15 keV Ga^+



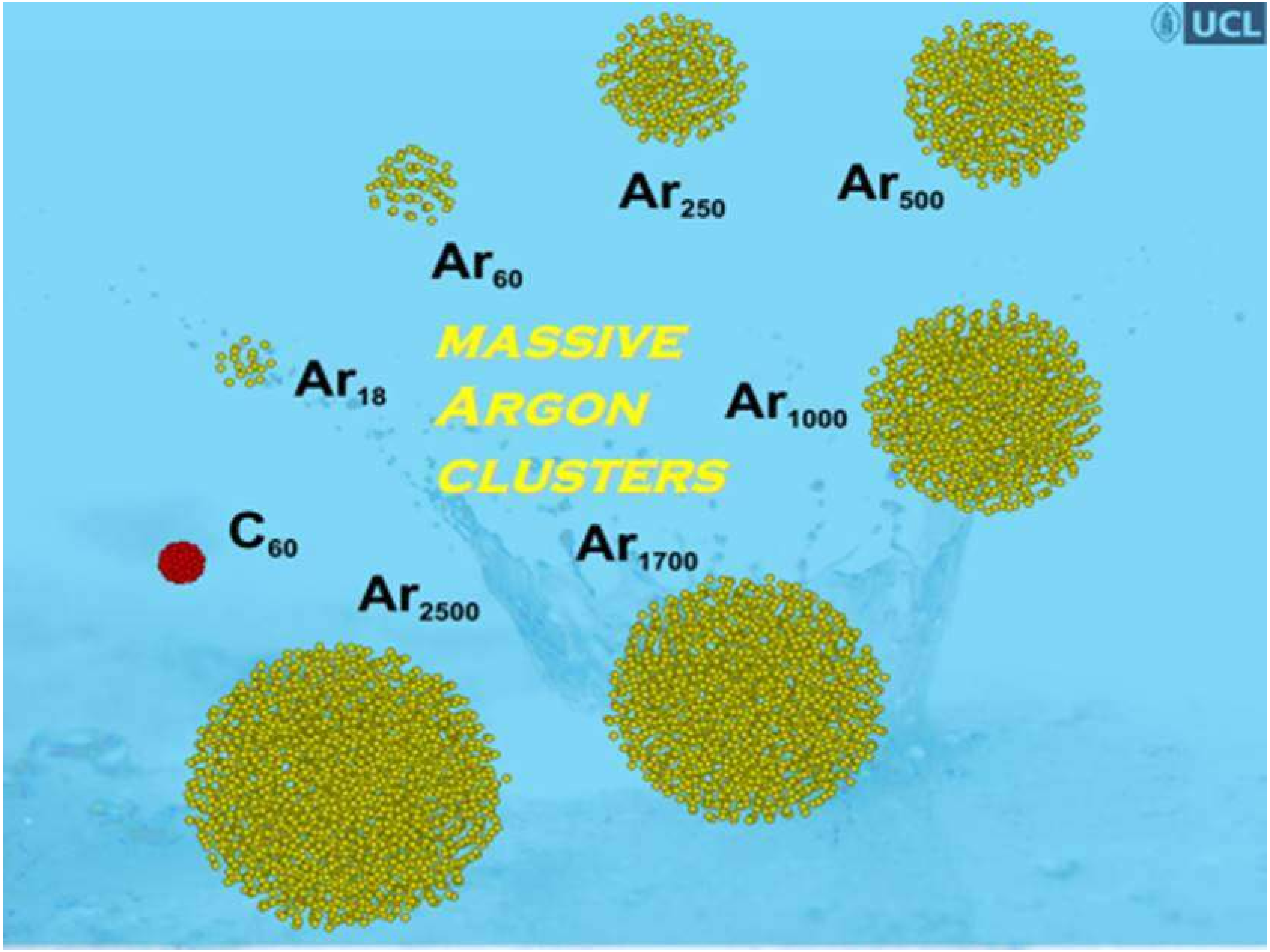
15 keV C_{60}^+

t=29 ps

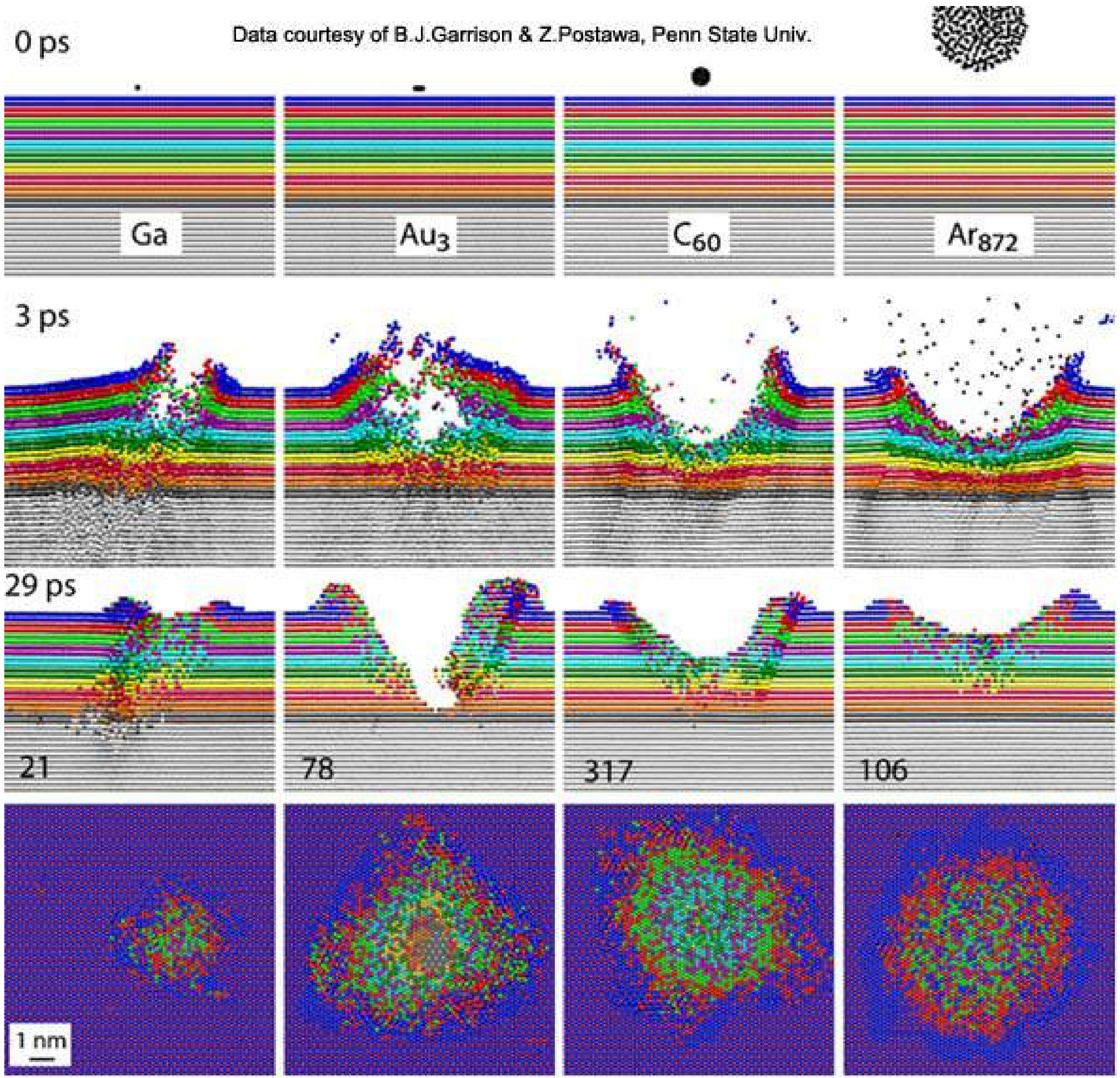


C_{60} bombardment calculations, Zbigniew Postawa; Enhancement of Sputtering Yields due to C_{60} vs. Ga Bombardment of Ag{111} as Explored by Molecular Dynamics Simulations, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, Anal. Chem., **75**, 4402-4407 (2003); Microscopic insights into the sputtering of Ag{111} induced by C_{60} and Ga Bombardment, *ibid*., J. Phys. Chem. B, **108**, 7831-7838 (2004).

Surface Chemical Analysis by XPS and SIMS

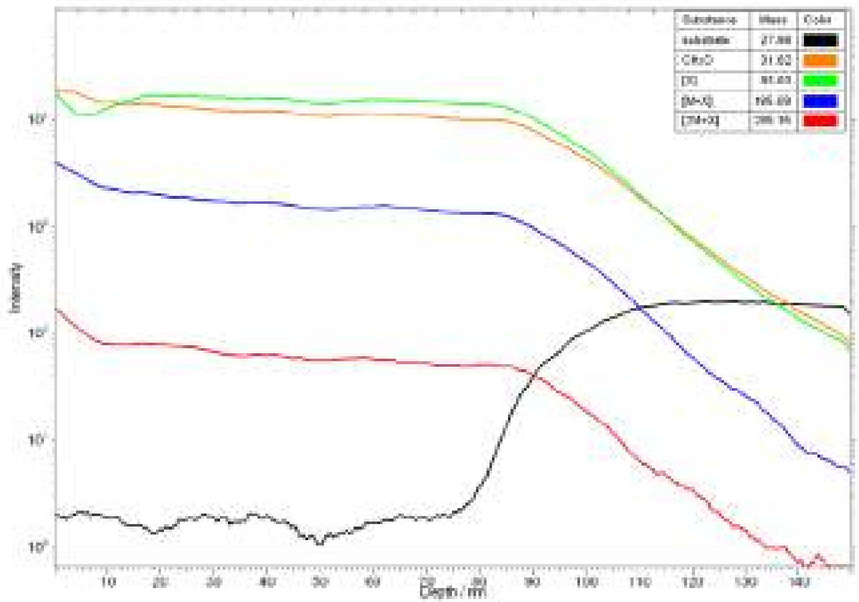


Surface Chemical Analysis by XPS and SIMS



Surface Chemical Analysis by XPS and SIMS

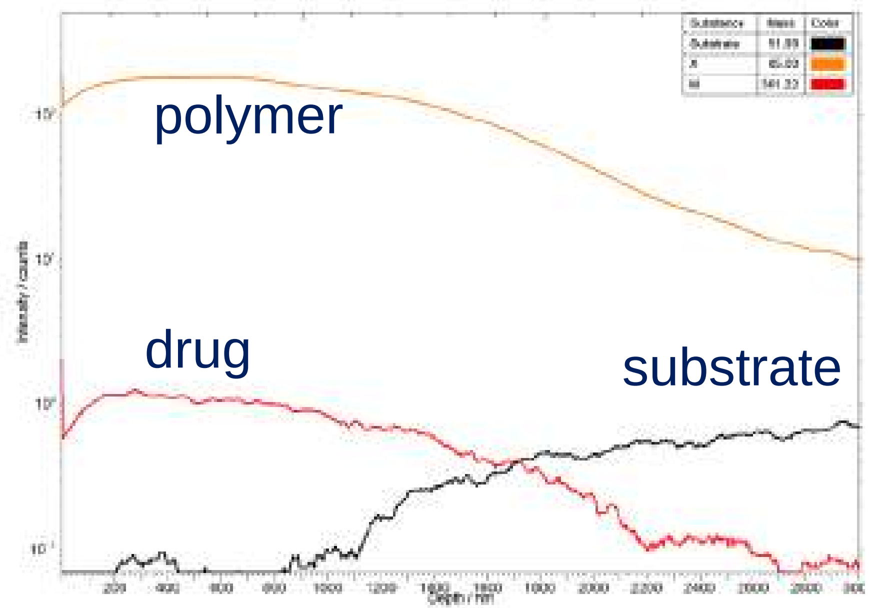
Depth profiling of organic materials using polyatomic ions Bi_x^{n+}, SF_5^+, C_{60}^+ Ar_{2500}^+



Thin polymer layer on Si substrate

~ constant signal from molecular species

Thick polymer coating containing drug on substrate



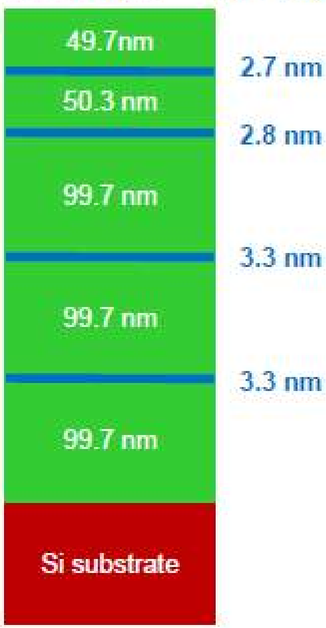
Modern Gas Cluster Ion Sources allow depth profiling through organic materials and devices with little or no damage to the molecular structures …

Sample: OML 03-I from NPL

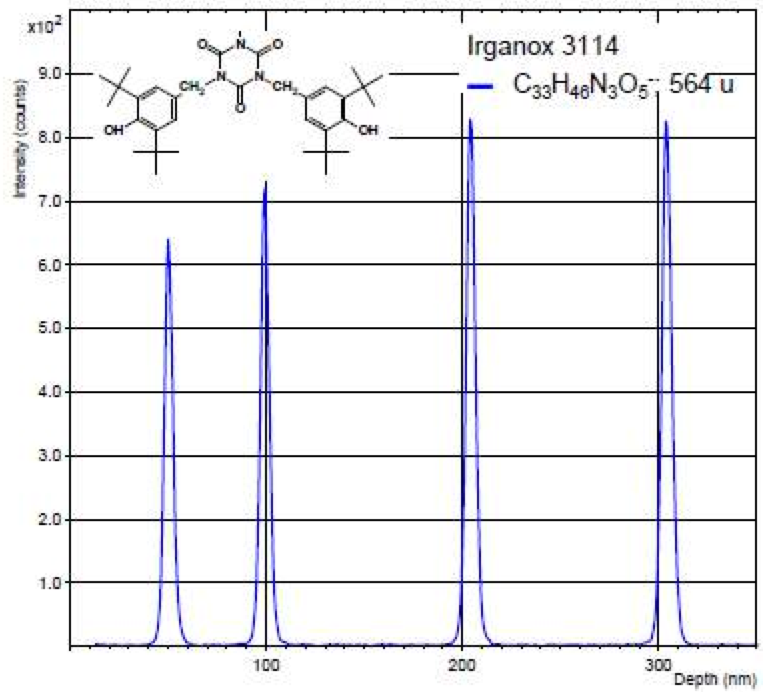
A.G. Shard*, R Foster, I. S. Gilmore, J. L. S. Lee, S. Ray, L. Yang
VAMAS Interlaboratory Study on Organic Depth Profiling

Irganox 1010
$C_{73}H_{108}O_{12}$
m = 1176 u

Irganox 3114
$C_{48}H_{69}N_3O_6$
m = 783 u

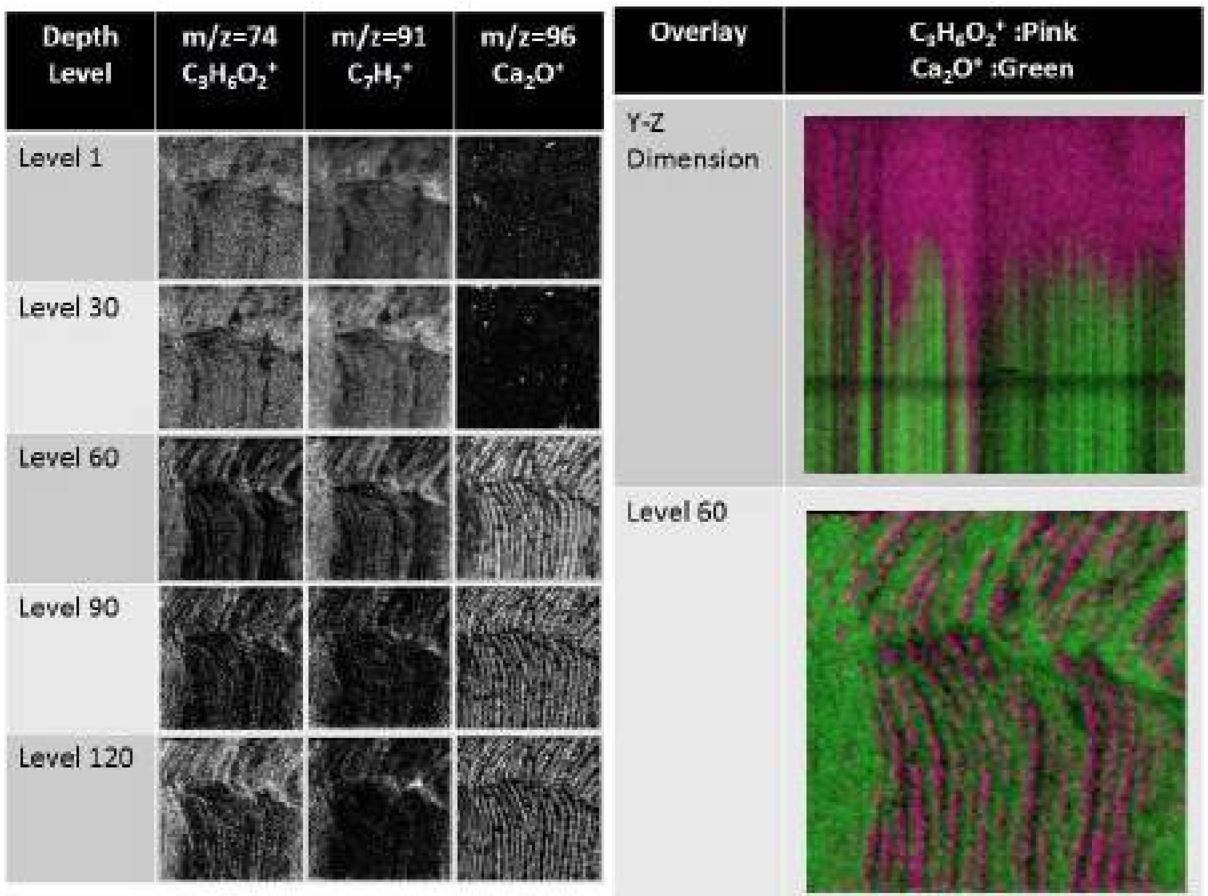


Analytical Conditions:
Sputtering: Ar_{1700}, 2.5 keV, 45°, rotation
Analysis: Bi_3



Surface Chemical Analysis by XPS and SIMS

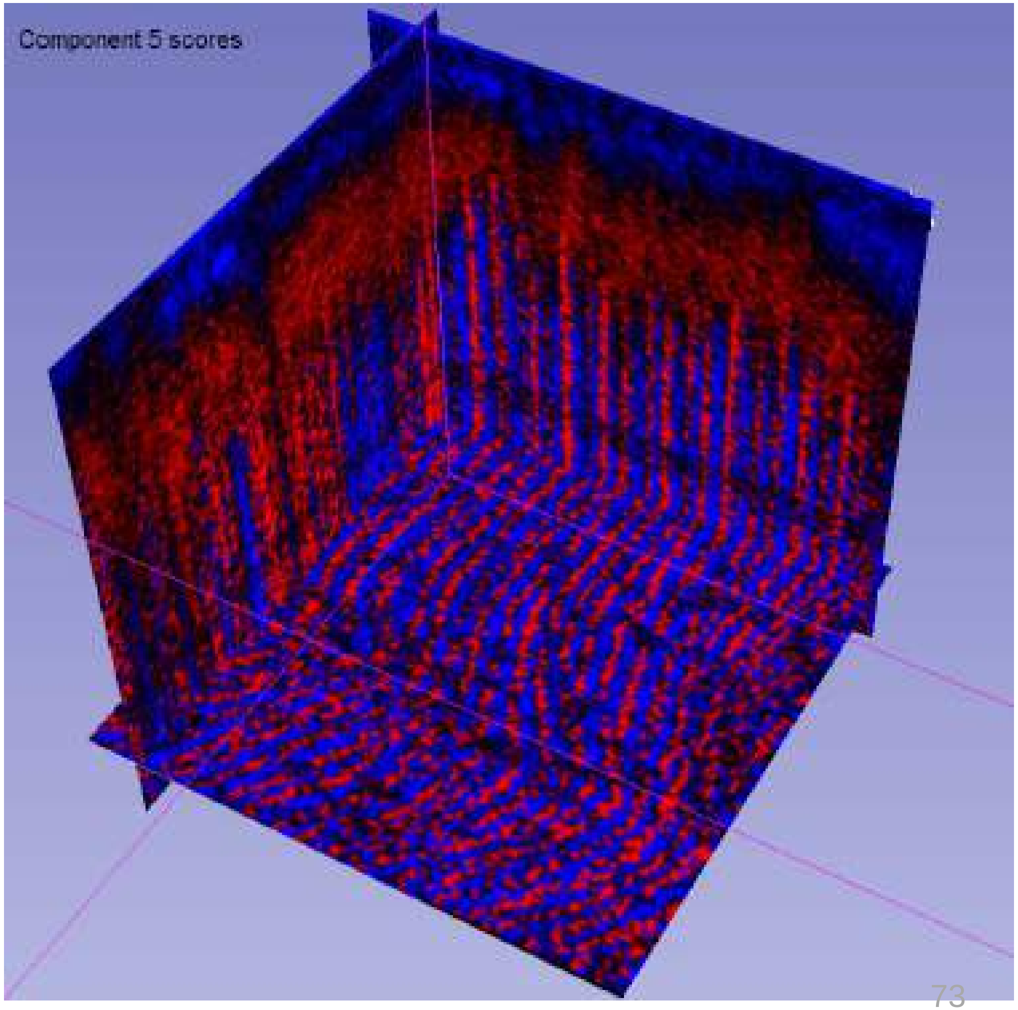
3D Imaging Static SIMS - Yucca plant leaf



Surface Chemical Analysis by XPS and SIMS

3D Imaging Static SIMS - Yucca plant leaf

- Full mass spectrum in each 2D pixel or 3D voxel
- Big datafiles: 1TB+
- Principal Component Analysis
- Usually a slow process
- New algorithm - PJC
- Very fast
- 10 seconds vs 27 hours
- Quickly screen data
- Reprocess to ID chemistry etc.
- Overall a very powerful toolkit!



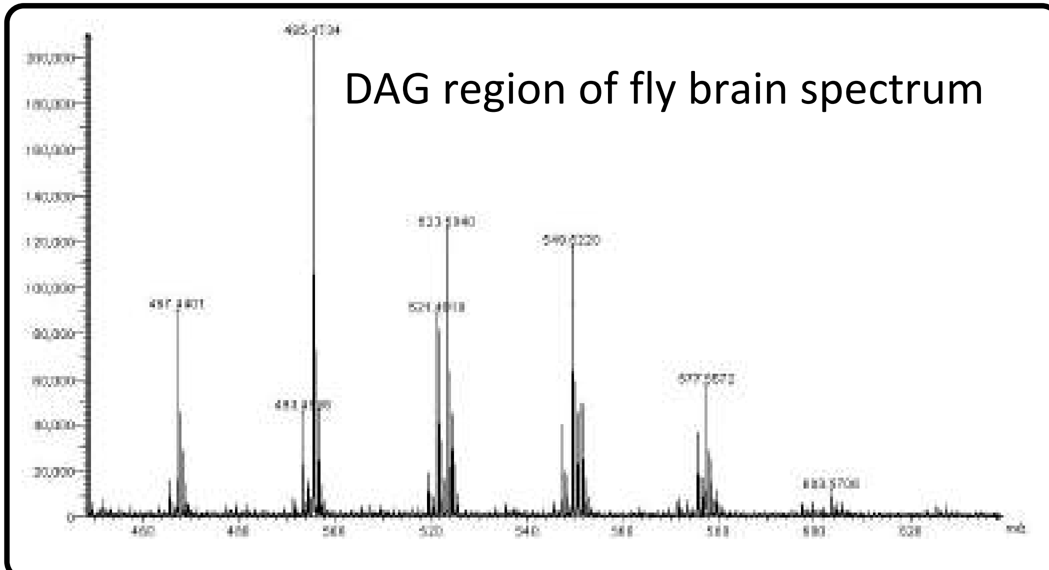
Latest developments .....

- $(H_2O)_{6000}^{+}$ cluster ion source
  - 10 to >100x more signal for protonated species compared to Ar_{4000}^{+}
  - 2 micron spatial resolution
  - lower detection limits
    - analysis of real therapeutic dose levels
    - trace analysis

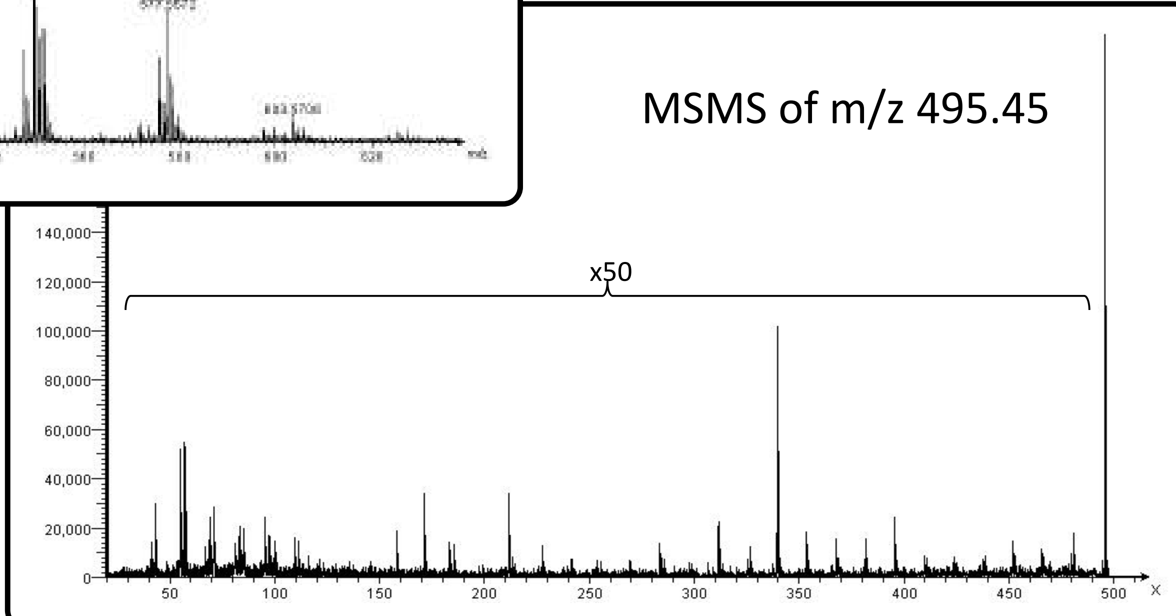
Latest developments …..

- Mass Spec – Mass Spec MSMS
  - Collision Induced Dissociation of secondary ion species produces spectra that are similar to 'normal' mass spectra
  - comparison with standard databases
  - facilitates identification / interpretation

MSMS of Diacylglycerides in Fly brain



High energy CID
(0.5 – 6 keV)
Nitrogen collision gas
ToF-ToF



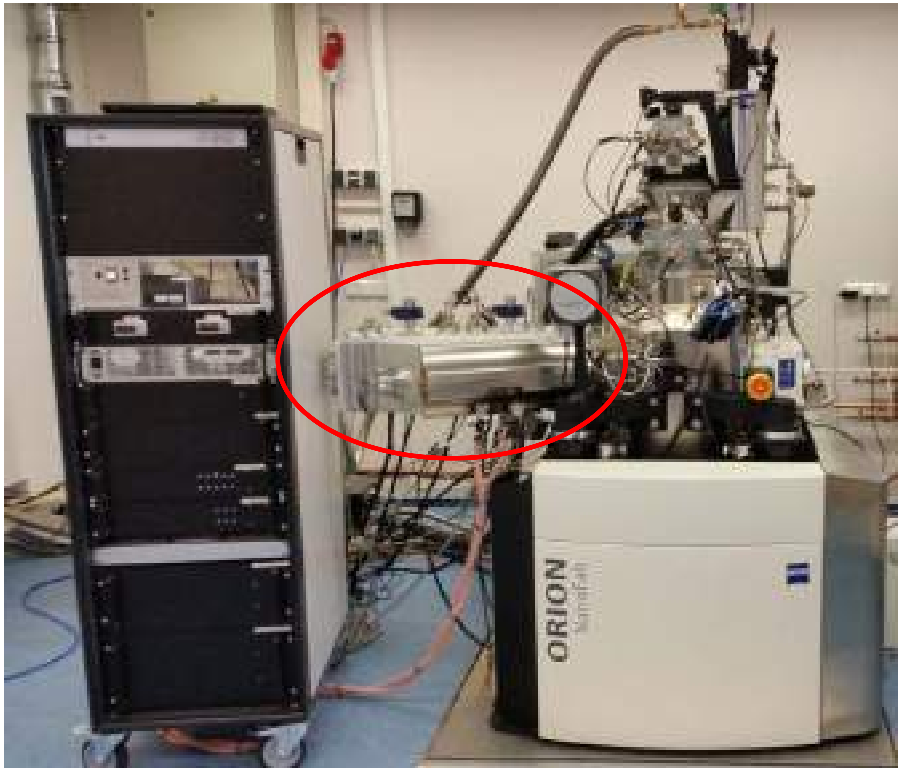
Povides detail on chain lengths and saturation and there increased specificity that tells us about the biology.

IONOPTIKA
ion beam technology

Surface Chemical Analysis by XPS and SIMS

Latest developments …..

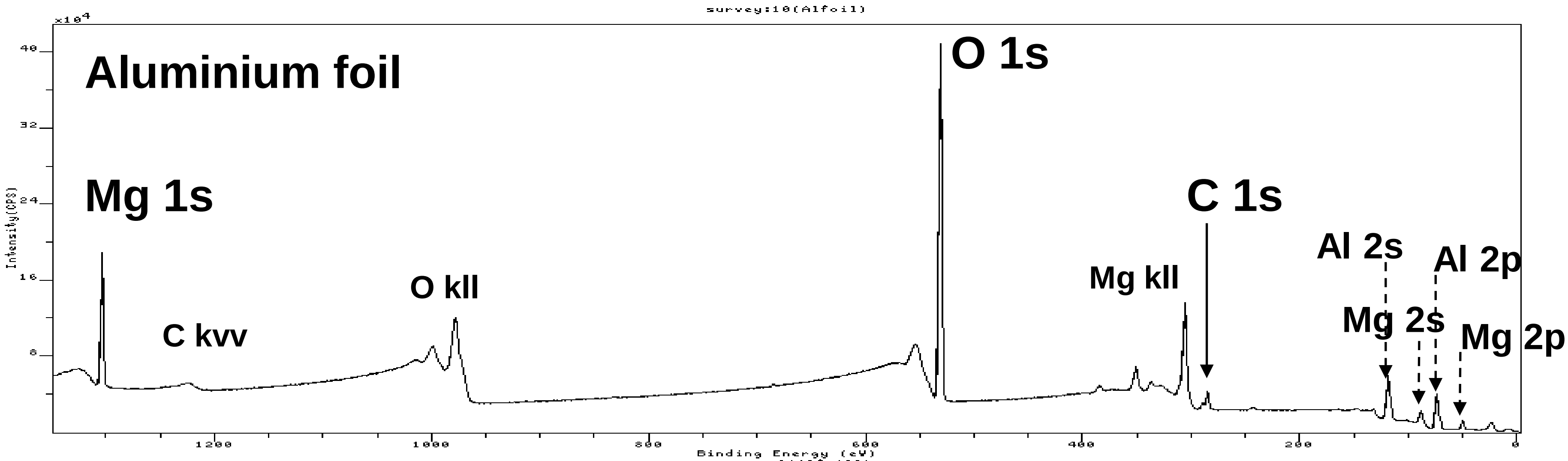
- 10nm spatial resolution
  - Magnetic Sector upgrade to Zeiss Orion HIM
  - Ne^{+} primary ions

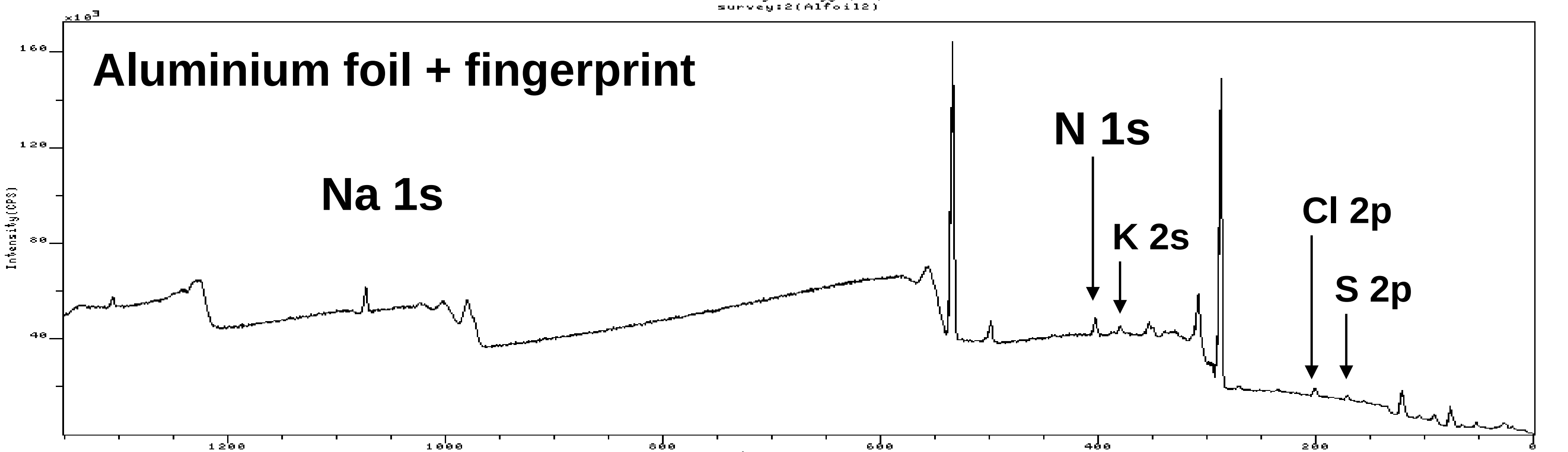


Examples of Applications

- Based on real examples and real data
- Some details changed to preserve confidentiality etc.

Surface contamination and cleaning





Surface contamination and cleaning

Relative Atomic Percentage Composition

	Al foil	Contaminated
Mg	5	0.2
O	58	24
C	10	65
Al	27	8
Na	-	0.8
K	-	1.1
Cl	-	0.6
S	-	0.4

Can't touch the sample for analysis!

Care also with sample packaging

Surface contamination and cleaning

Ag foil used for adhesive developments

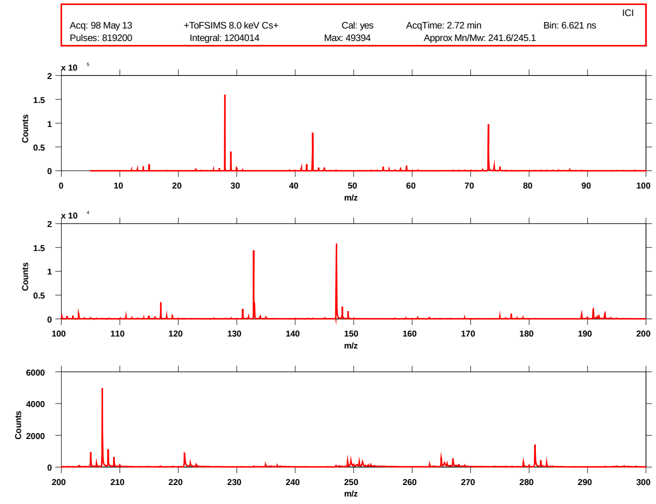
	Rel. At. % Comp		
	Ag	C	O
As received	51	40	9
Solvent wipe	0.2	85	15
Solvent wipe + rinse	0.3	85	15
Ultrasonic washing	35	43	22

Polymer surfaces more favourable than metals, but beware:

- Solvent purity / contamination
- Plastic wash-bottles
- Contaminated glassware
- Extractables in tissues / cloths etc.

Poly(dimethylsiloxane), PDMS

$$
\begin{array}{c}
CH_3 \\
| \\
(\ \text{-}\ Si\ \text{-}\ O\ \text{-}\ )_n \\
| \\
CH_3
\end{array}
$$

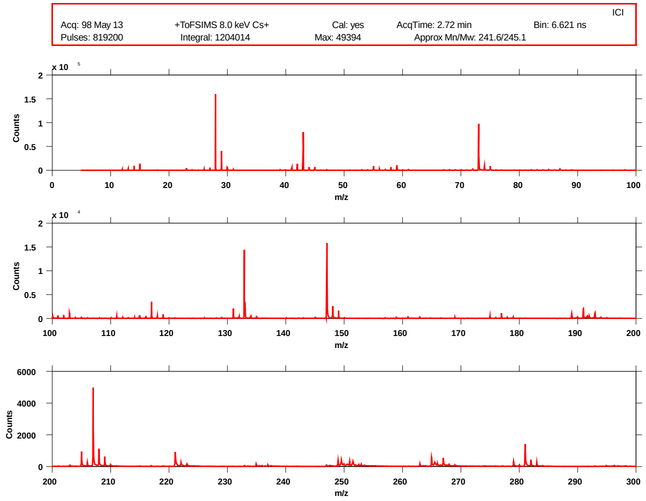


- very common family of materials
- many applications (lubricant, release agent, anti-foamer………)
- mobile, spreads easily
- cannot easily distinguish siloxanes from silicates by XPS
- very characteristic SSIMS spectra

- enough silicone manufactured to cover the surface of the Earth to a level of several nm deep!

Poly(dimethylsiloxane), PDMS

$$\left(-\,\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}\,-\,O\,-\right)_n$$

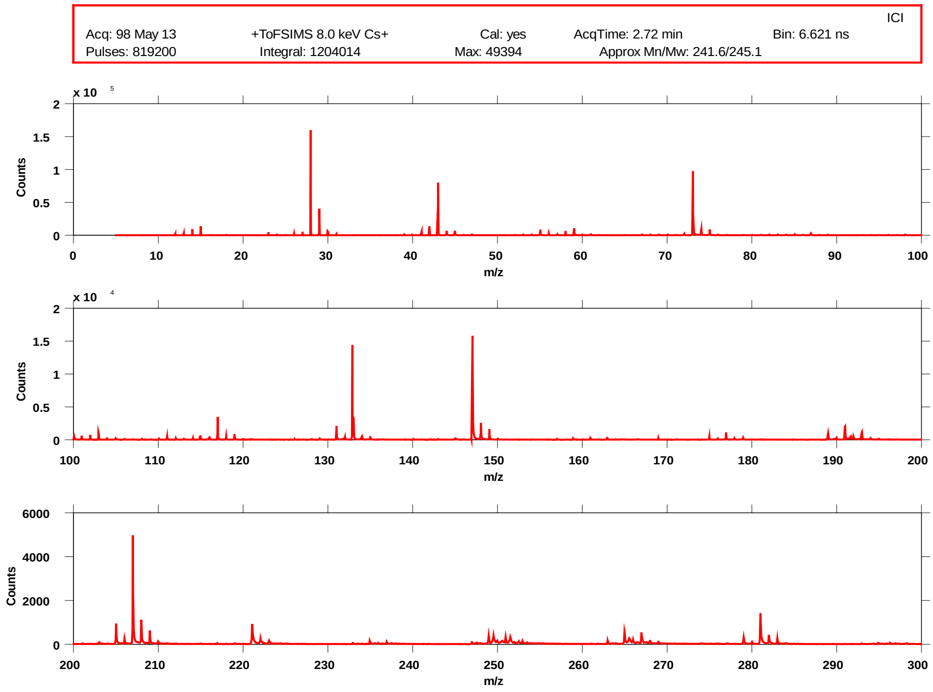


Typical example

- Polymer material used in adhesive application
- One ‘Good’ sample, one ‘Bad’
- Why?
- XPS: 10% Si on Good, 20% on Bad!! (Pure PDMS = 25% Si)
- SSIMS: dominated by PDMS signal

'Oily rag' syndrome

- Streaks and smears on extruded product ….
- Extruder lips cleaned with a proprietary domestic spray cleaner
- 'Silicone free' according to manufacturer

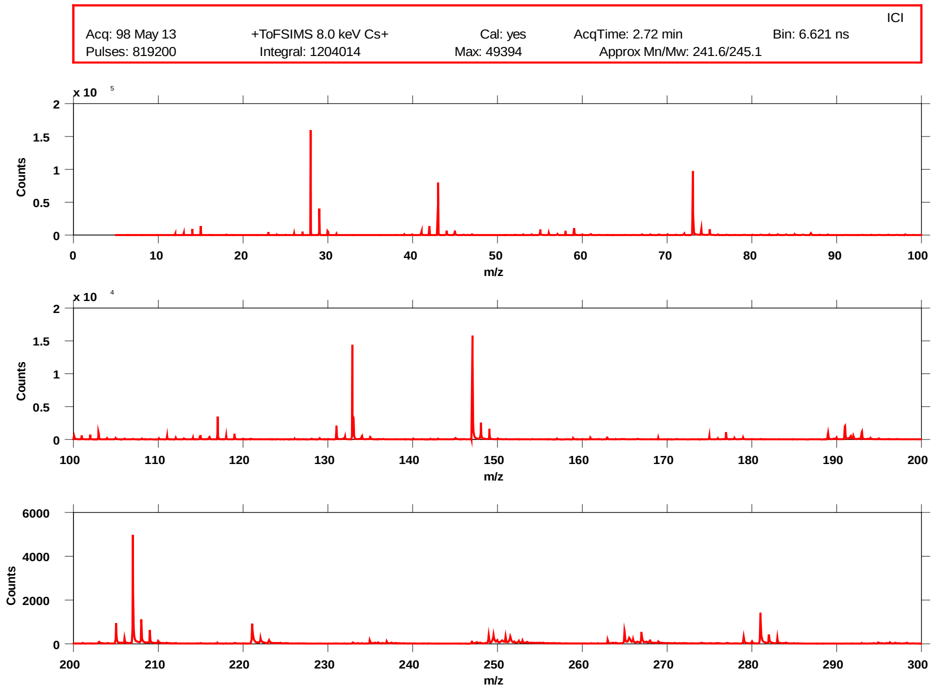


Surface Chemical Analysis by XPS and SIMS

‘Oily rag’ syndrome

- **Streaks and smears on extruded product ….**
- **Extruder lips cleaned with a proprietary domestic spray cleaner**
- **‘Silicone free’ according to manufacturer**

- **Anti-foam additive**

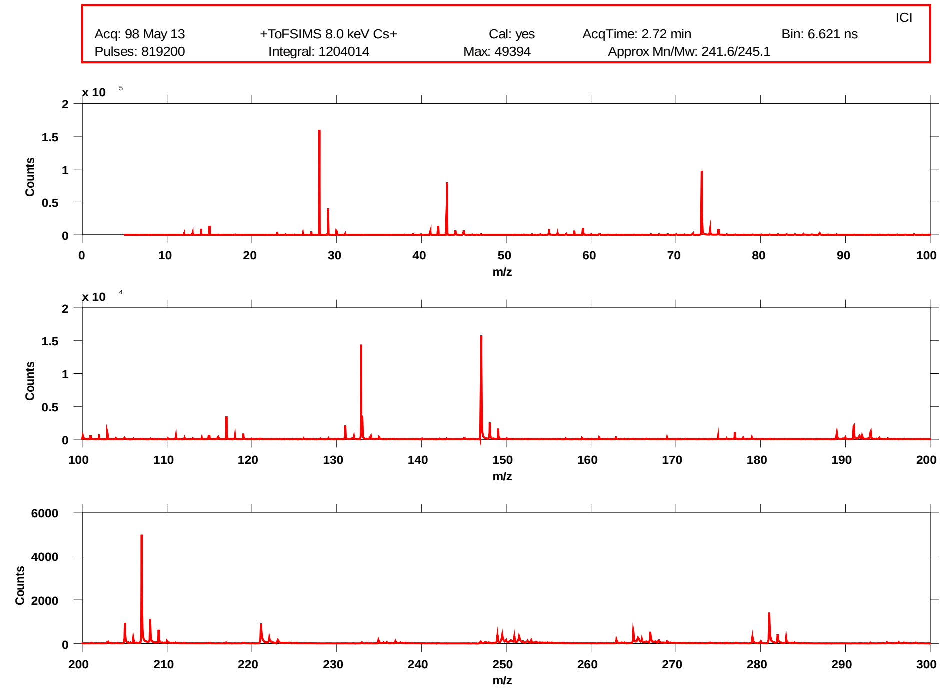


‘Oily rag’ syndrome

- **Streaks and smears on extruded product ….**
- **Extruder lips cleaned with a proprietary domestic spray cleaner**
- **‘Silicone free’ according to manufacturer**

- **Anti-foam additive**

- **Always shoot the man with the oily rag!**



Surface Chemical Analysis by XPS and SIMS

‘Oily rag’ syndrome

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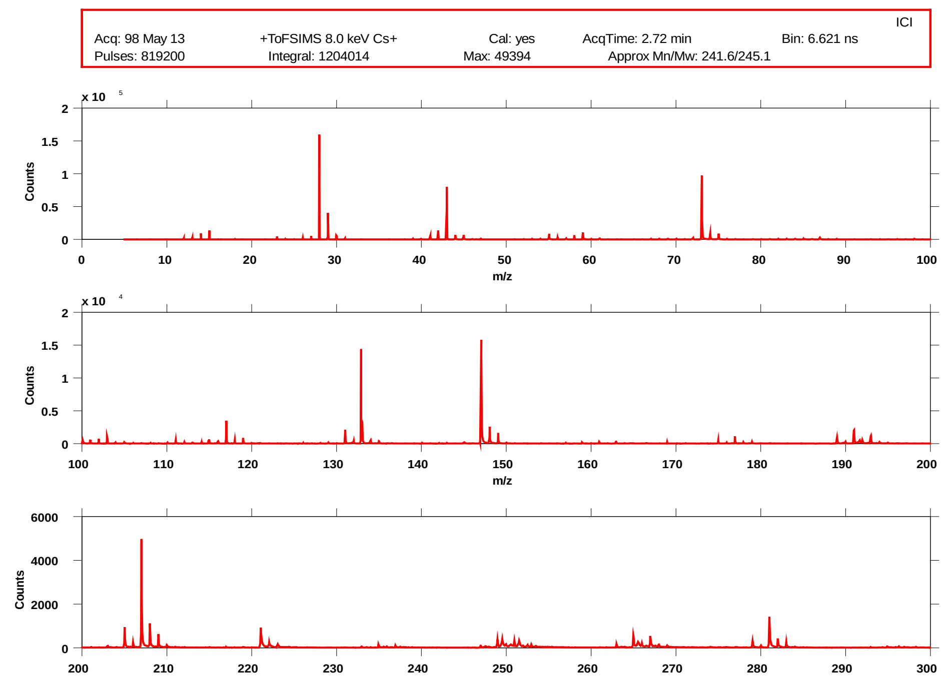
- Anti-foam additive

- Always shoot the man with the oily rag!
- Cleanroom example ….



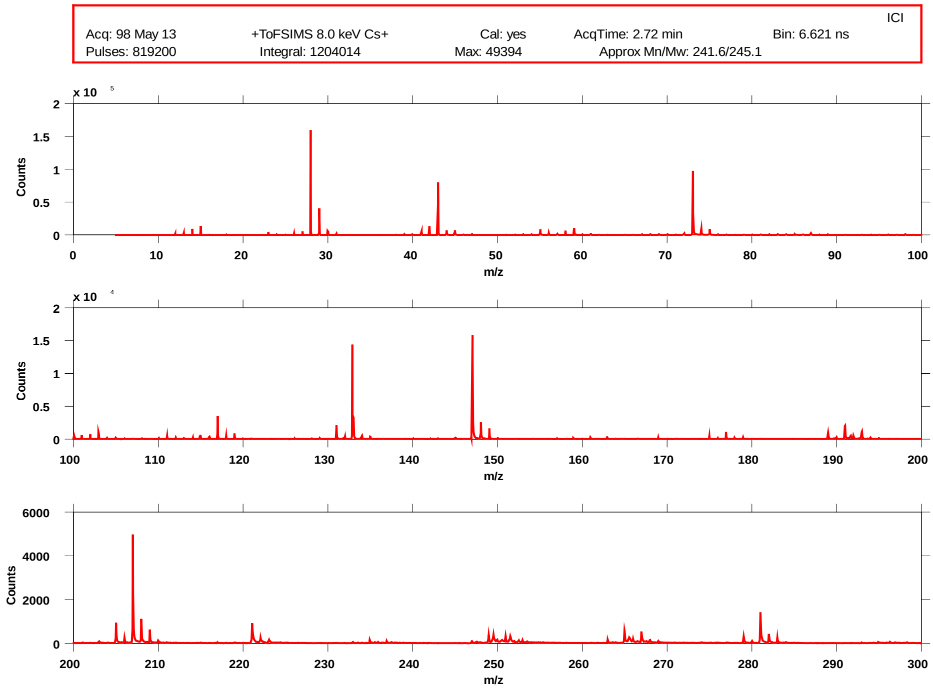
Surface Chemical Analysis by XPS and SIMS

'Oily rag' syndrome

- Streaks and smears on extruded product ….
- Extruder lips cleaned with a proprietary domestic spray cleaner
- 'Silicone free' according to manufacturer

- Anti-foam additive

- Always shoot the man with the oily rag!
- Cleanroom example ….
- Aerospace example ….

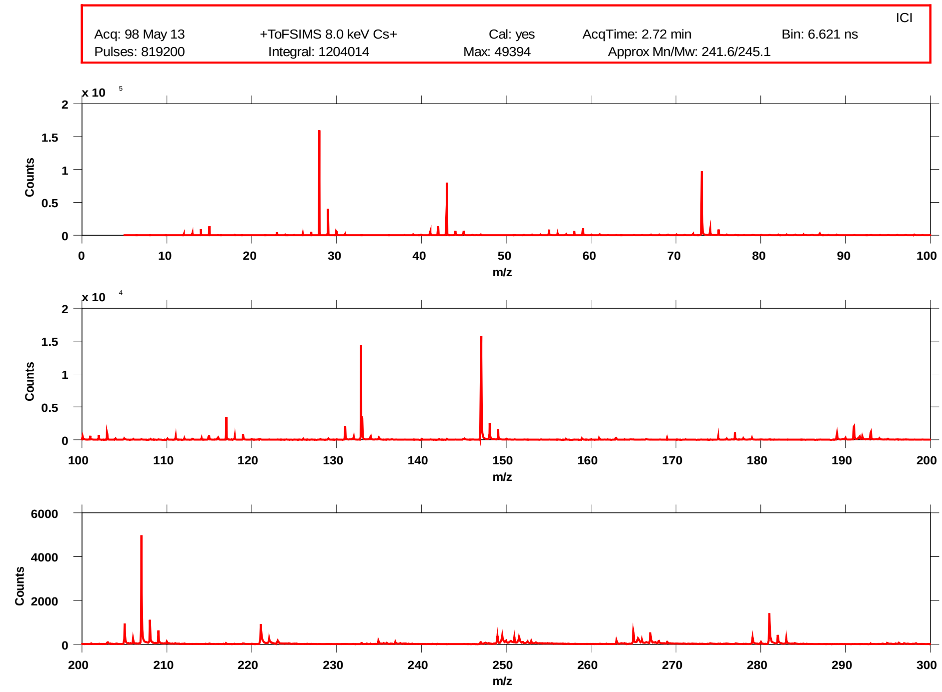


'Oily rag' syndrome

- Streaks and smears on extruded product ….
- Extruder lips cleaned with a proprietary domestic spray cleaner
- 'Silicone free' according to manufacturer

- Anti-foam additive

- Always shoot the man with the oily rag!
- Cleanroom example ….
- Aerospace example ….
- Automotive example ….

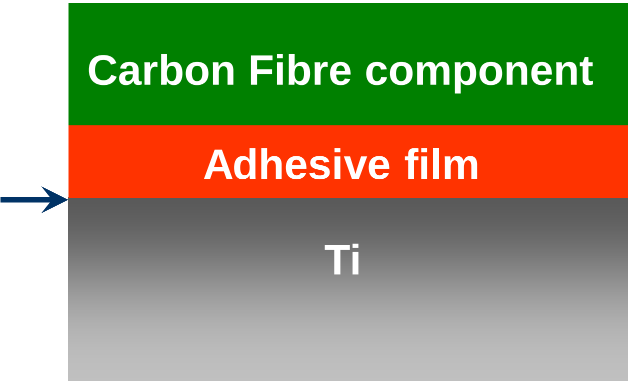


Surface Chemical Analysis by XPS and SIMS

High speed failures of novel suspension component

- 3 major testing accidents at 170mph+
- adhesive failure between CF and Ti components
- cause traced to inadequate cleaning of machined Ti
- fixed in time for the final races of 2001 season
- won the race & Drivers and Constructors championships

- new suspension design also used in 2002, 2003, 2004……



Not only fingerprints and PDMS, but also

- hydrocarbons
- fluorocarbons
- amides
- anti-oxidants
- UV stabilisers
- mould release agents
- surfactants
- mobile additives
- oligomers
- particulates
- …..

- one man's product is another man's contaminant

Failed coating example

- high-end vehicle doors – extra holes in the door panel cut by hand to fit new lock design
- painted as normal
- paint blisters forming after several months service …..

- ToFSIMS analysis from underside of paint flake
  - traces of original cutting fluid
  - inadequate cleaning after cutting

Failed coating example

- internal coating on pipework failing leading to corrosion
- offshore application – expensive and difficult to repair
- repeating pattern noticed every few metres along the pipe ……

- ToFSIMS analysis
  - traces of high pressure hydraulic oil between the coating and the steel pipe surface
  - pipe manufacturing process issue identified

Failed coating example

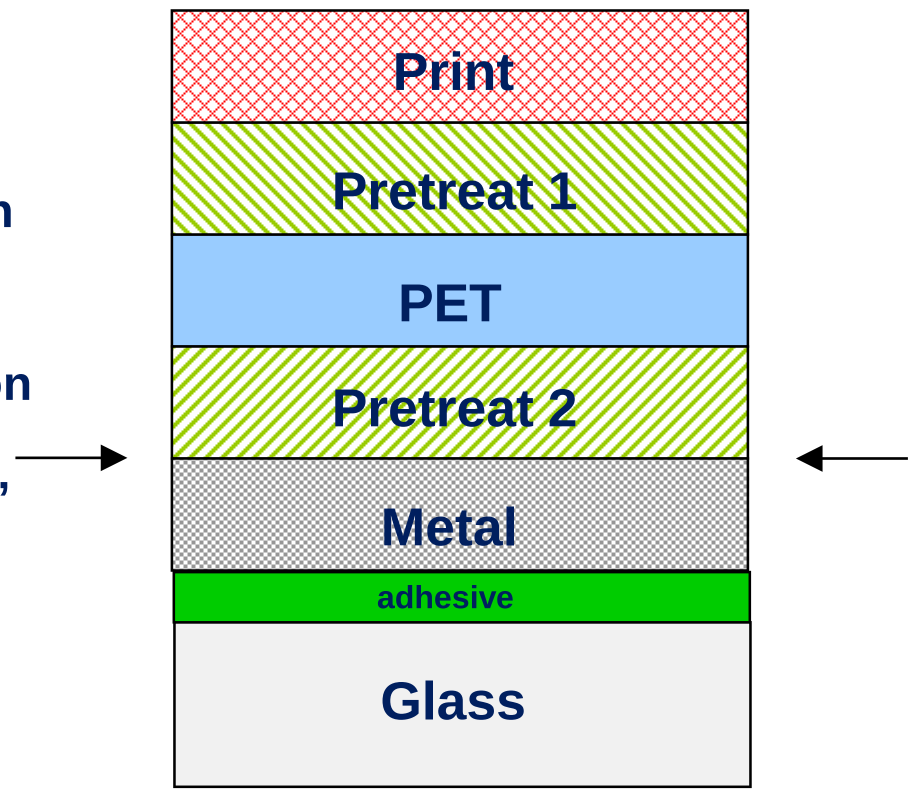
- Bottle label falling off during re-use washing cycle
- expected sequence: wash / rinse / remove label

Pretreat 1 optimised for print adhesion

Pretreat 2 optimised for metal adhesion

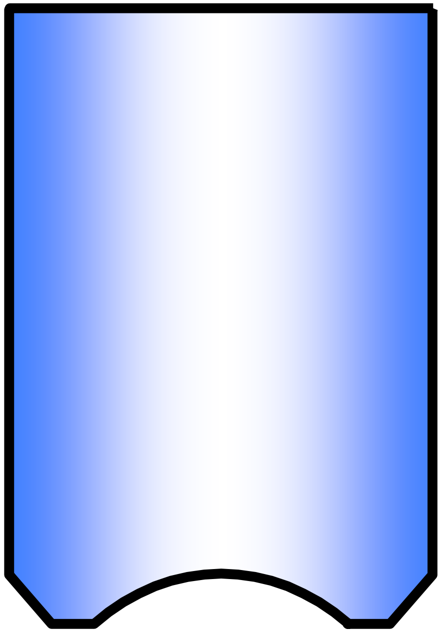
Failure between metal and pretreat “2”

Why?



XPS / SIMS analysis of a coated can

- metal processing
- cleaning
- inner coating
- outer coating
- printing
- lacquer



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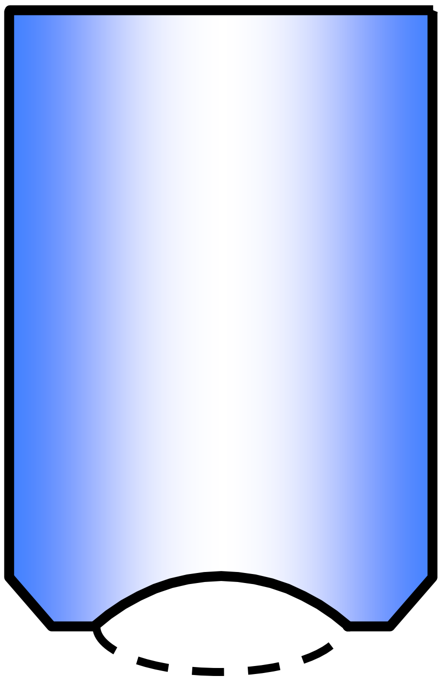
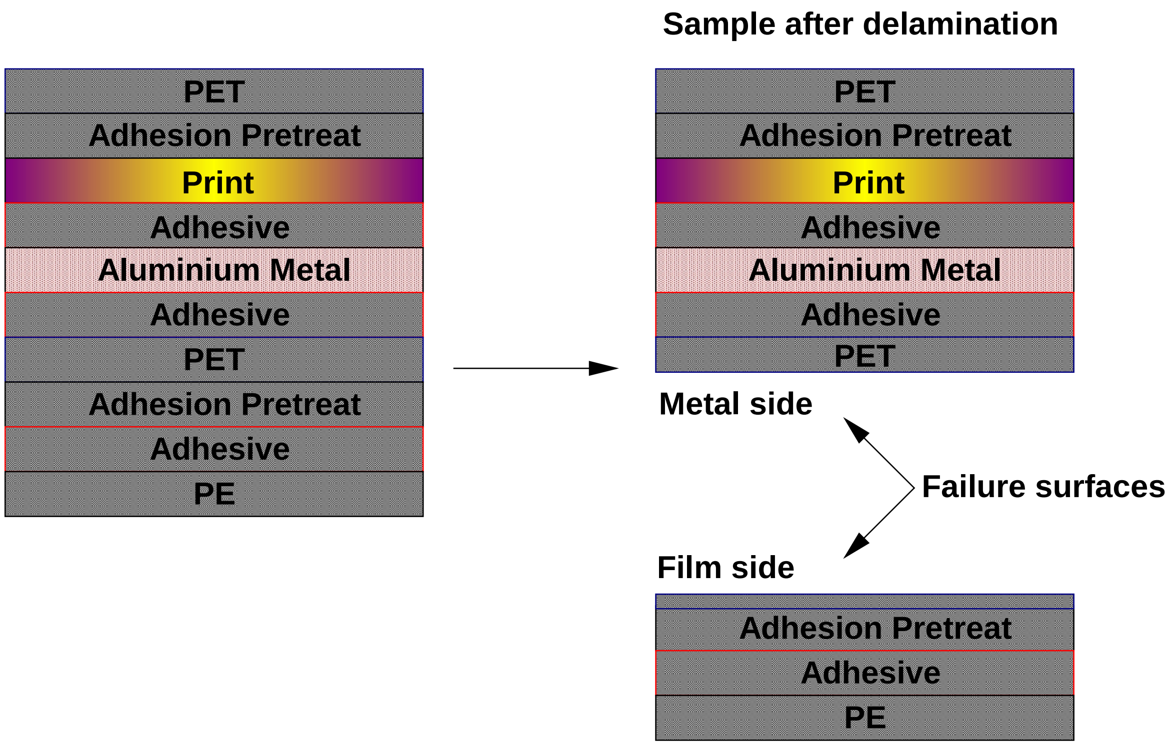


Plane of failure analyses

- Packaging laminate



Identification of an Unknown Green Slime by XPS!

- Urgent problem - what is it and where did it come from?
- Sample dried in air at 50°C for 1 hour

Sample	Relative Atomic Percentage Composition			
	C	S	O	Cr
Unknown	64.4	8.2	24.7	2.7
Cr Tosylate	61.8	8.8	26.5	2.9

Significant aromatic character in C1s spectrum
O:S ratio ~ 3:1
S:Cr ratio ~ 3:1
Cr as Cr III, S oxidised, sulphate or sulphonate-like

Overall, results consistent with: $(CH_3\text{-}C_6H_4\text{-}SO_3^-)_3Cr$

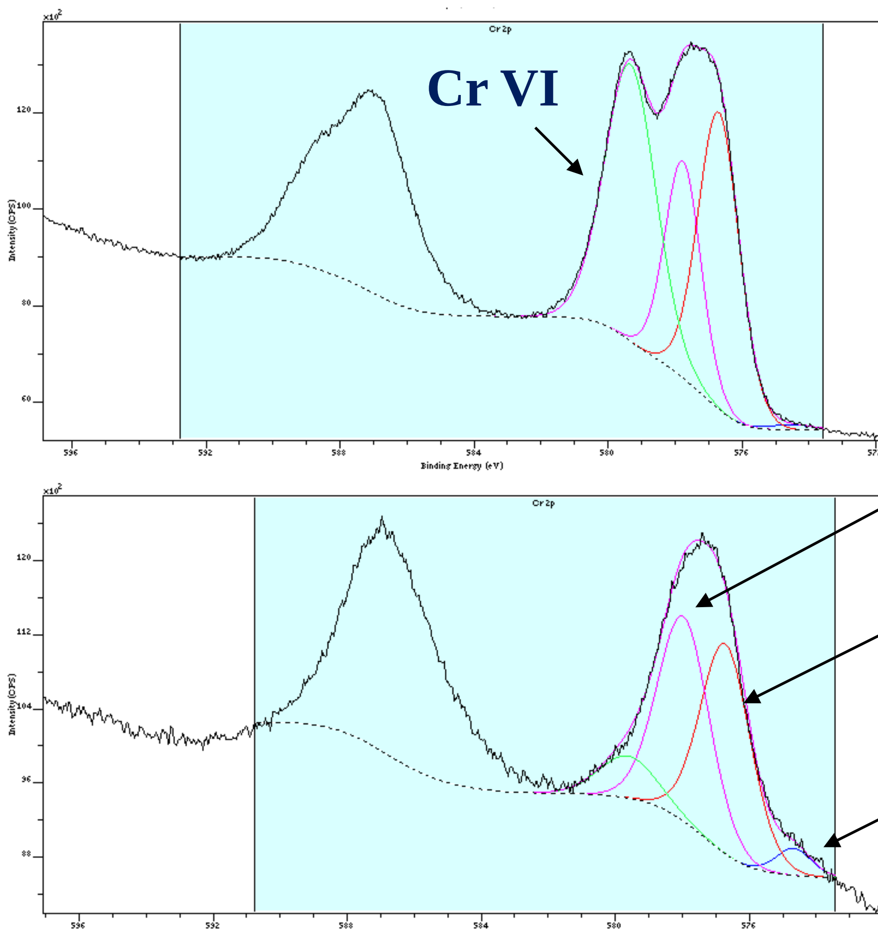
Determination of Cr VI content by XPS

Cr 2p high resolution spectra

XPS data:

11% Cr
40% as Cr VI

6% Cr
10% as Cr VI



Sampling depth 3-5nm

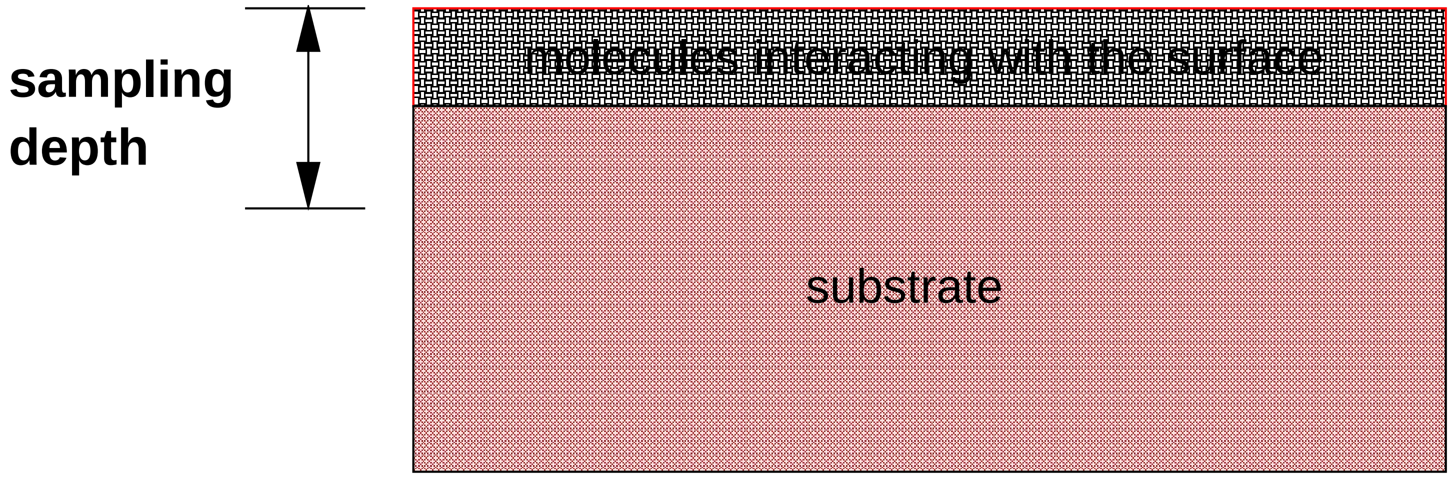
$Cr(OH)_3$

Cr_2O_3

Cr metal

Overlayer - substrate interactions

- Compare thin layer with a relatively thick layer
- Overlayer thickness determination



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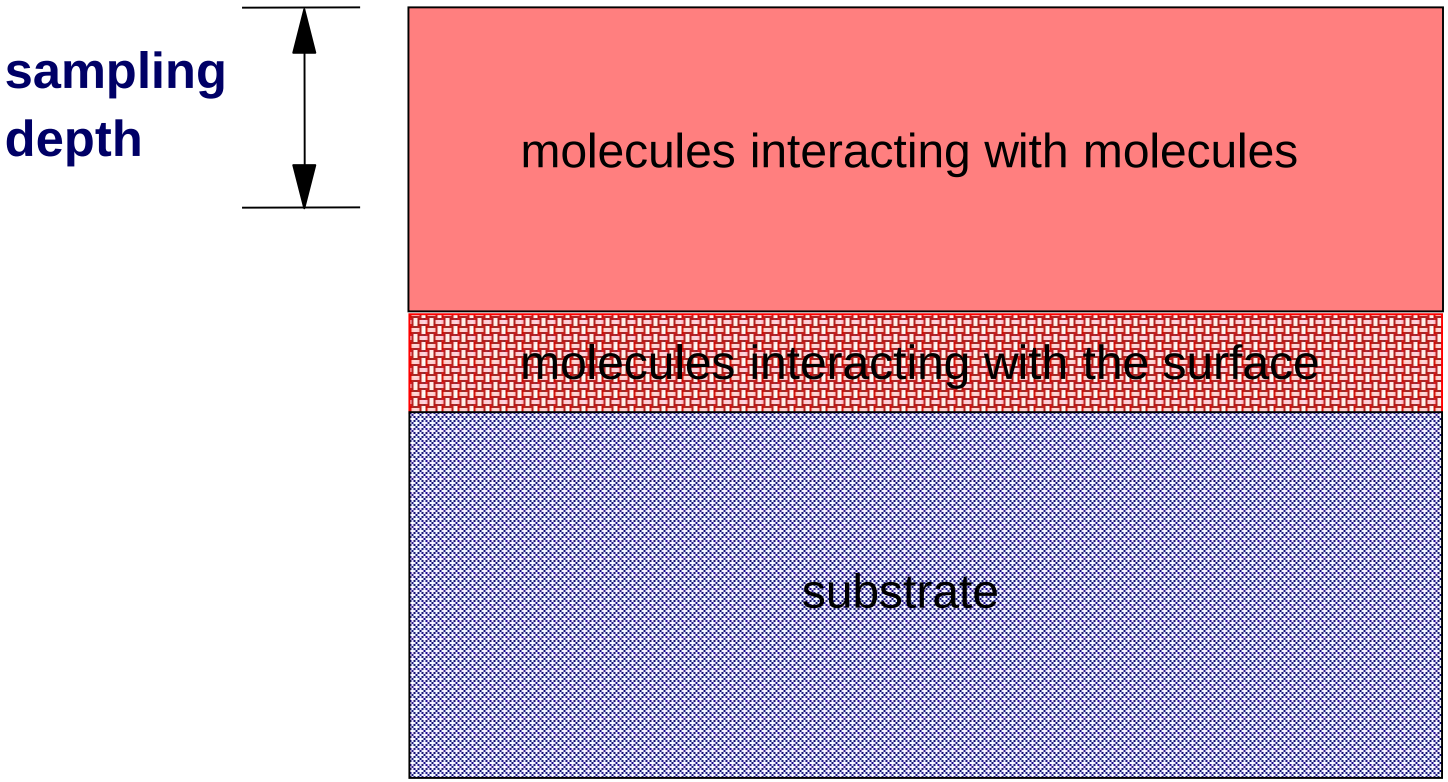


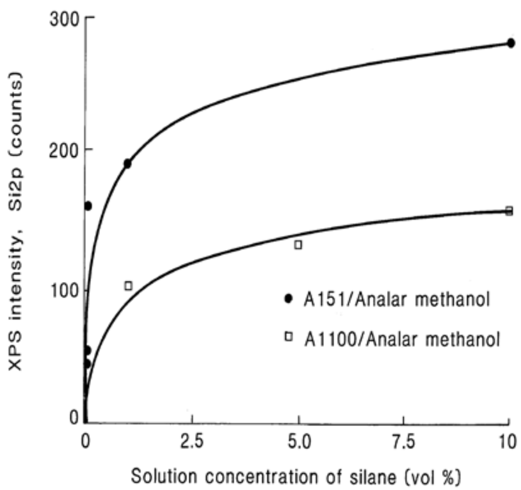
Bond Type	Energy/kJmol^{-1}
Ionic	600-1100
Covalent	60-700
Metallic	110-350
Brönsted Acid-Base	Up to 1000
Lewis Acid-Base	Up to 80
Hydrogen Bonds (incl F)	Up to 40
Hydrogen Bonds (excl F)	10-25
Permanent Dipole-Dipole	4-20
Dipole-Induced Dipole	< 2
Dispersion Forces	0.08-40

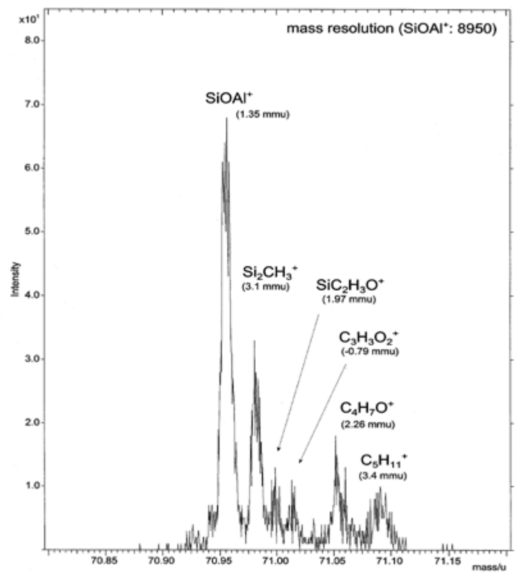
primary bonds ↔ secondary bonds

van der Waals bonds

Adsorption Isotherms

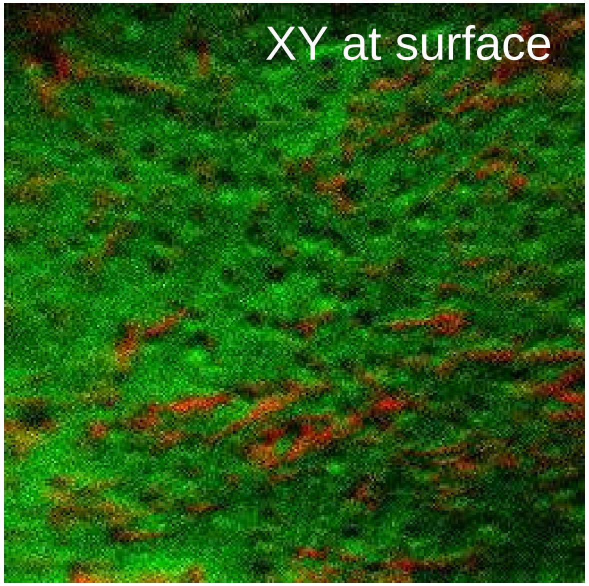
- XPS provides reliable quantitative surface chemical analysis
- ToF-SIMS provides semi-quantitative molecular data
- Both can be used to estimate density of bonding sites and bond type



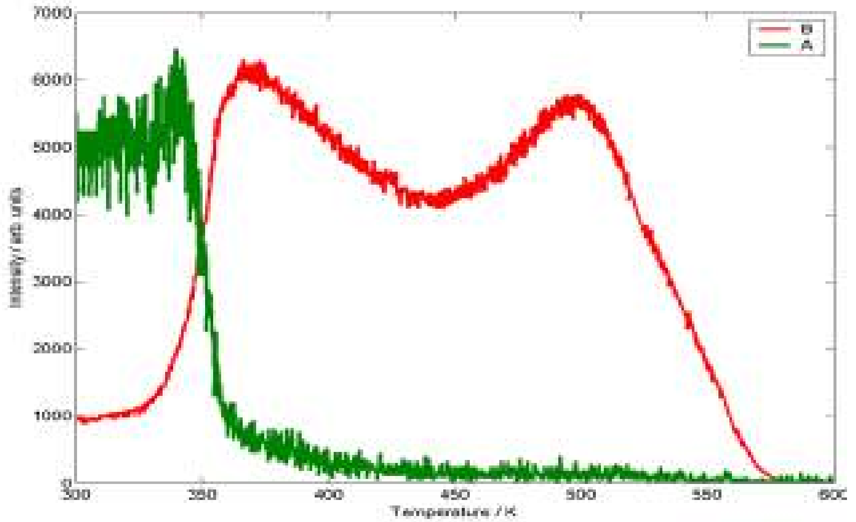


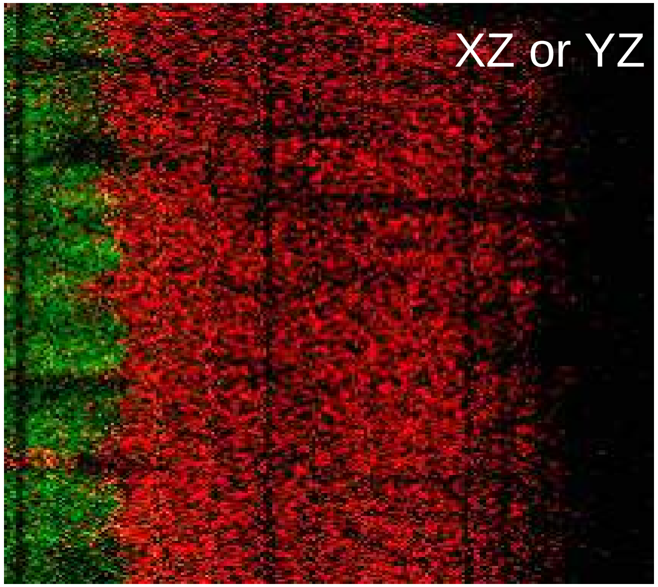
Surface Chemical Analysis by XPS and SIMS

"Thermal Desorption" SSIMS



500µm x 500µm

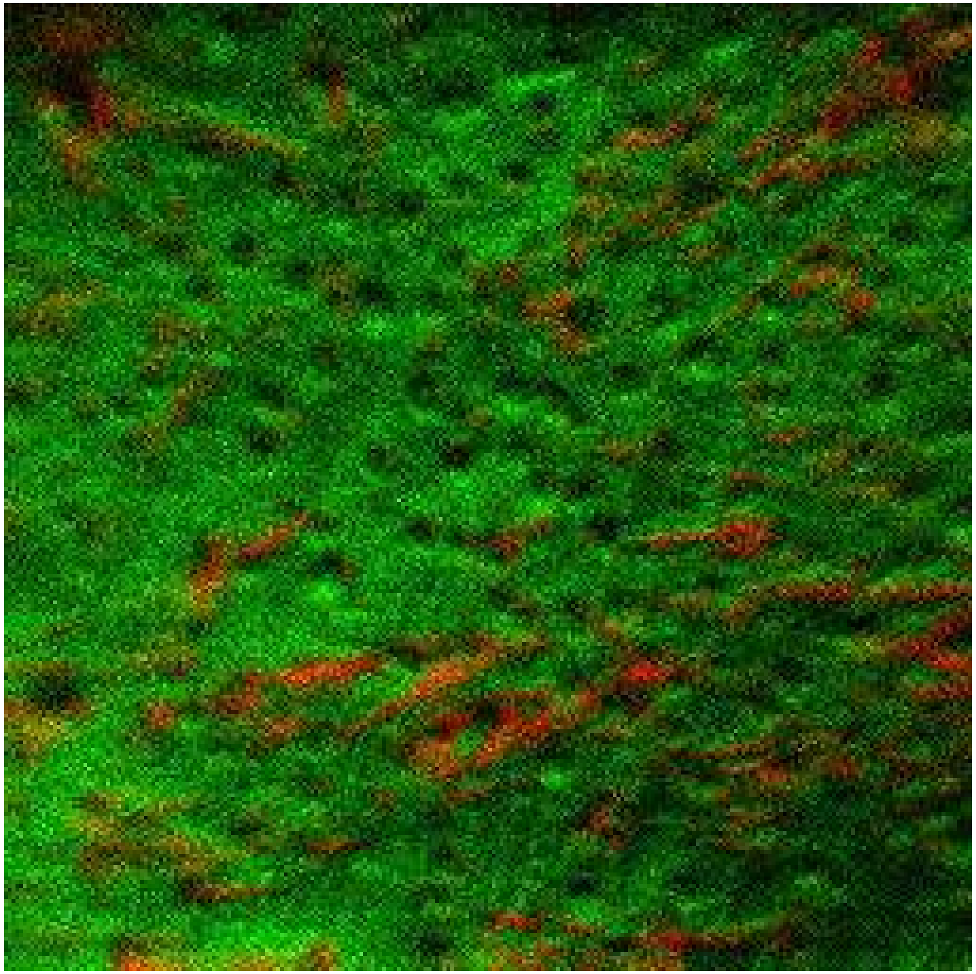




Treated Metal Surface

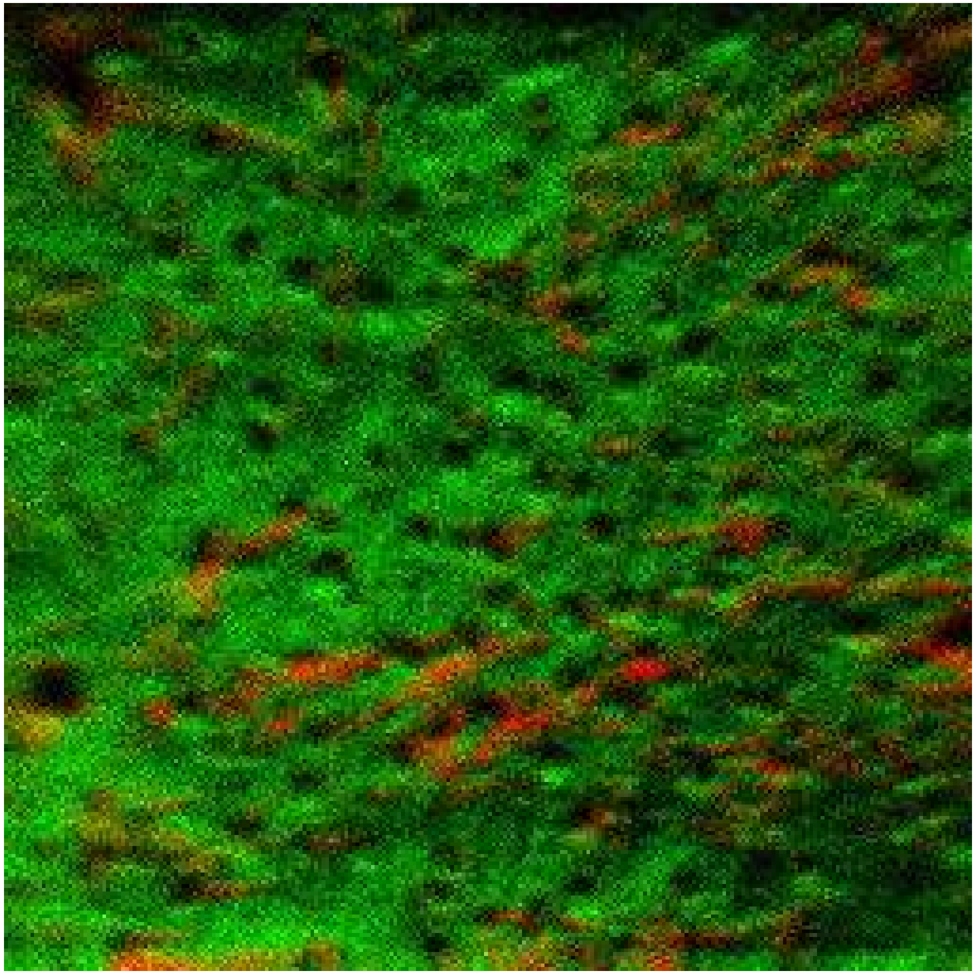
- 2 additives A and B
- competitive adsorption onto metal surface
- ~4 nm thick layer
- TD SSIMS analysis from 30 - 400 °C
- use of molecular ions for each additive
- estimate desorption energies from T at the maximum rate of desorption

Surface Chemical Analysis by XPS and SIMS



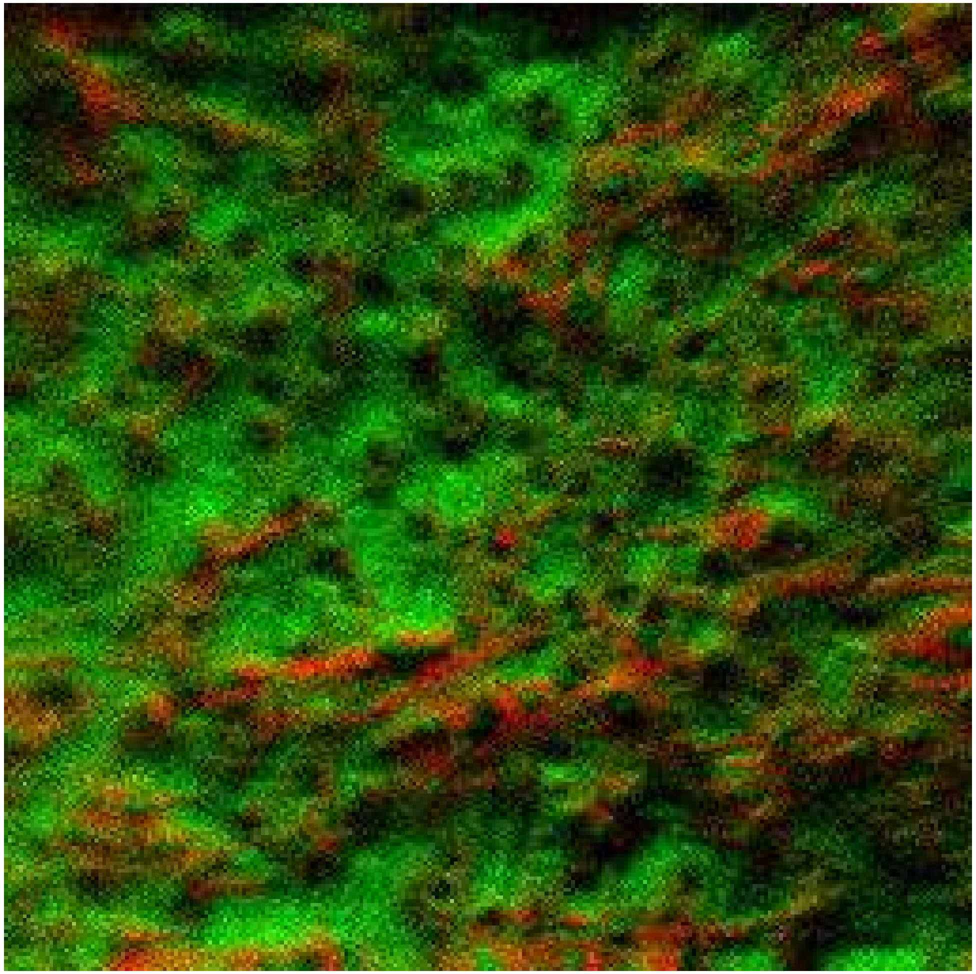
45 °C

Surface Chemical Analysis by XPS and SIMS



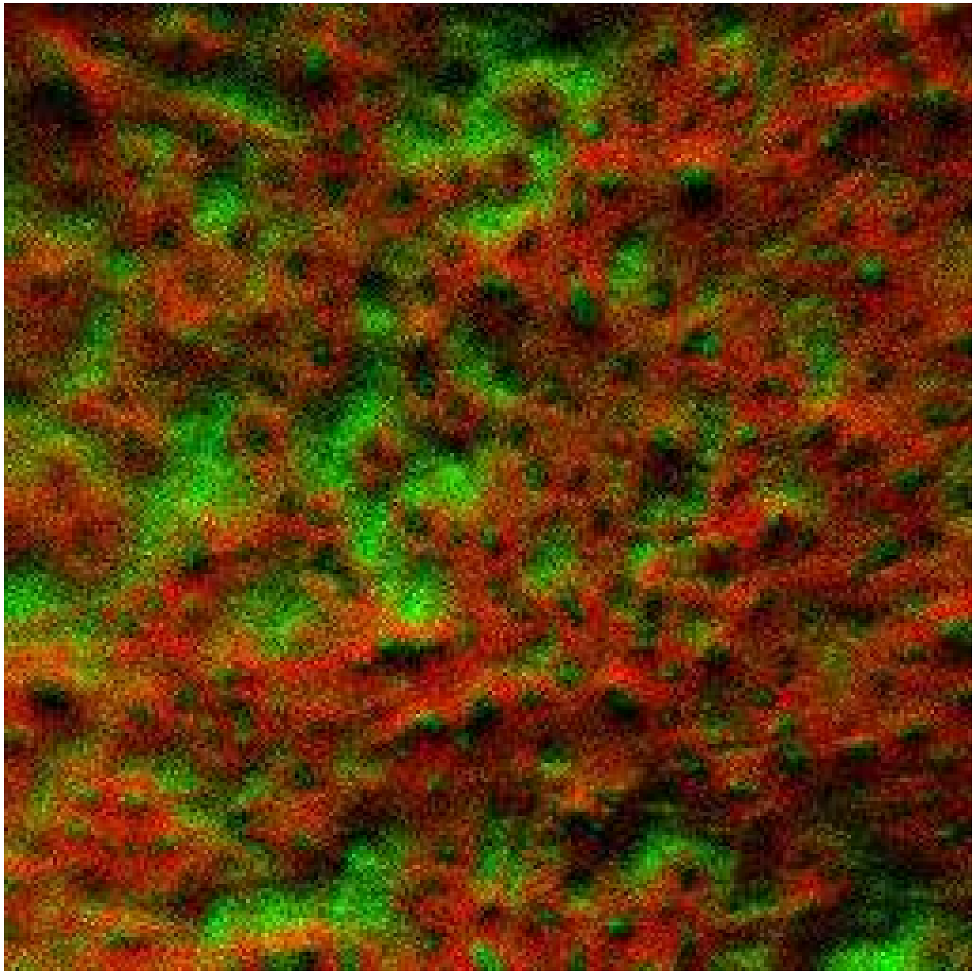
60 °C

Surface Chemical Analysis by XPS and SIMS



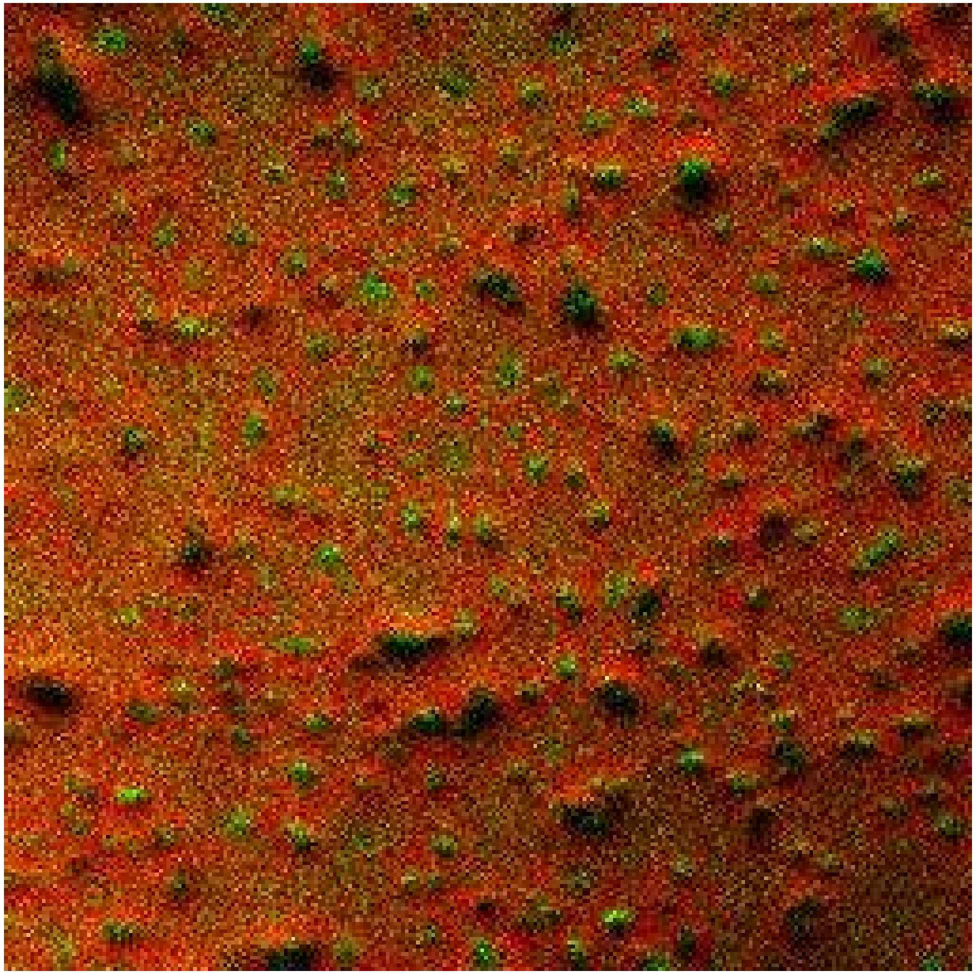
75 °C

Surface Chemical Analysis by XPS and SIMS



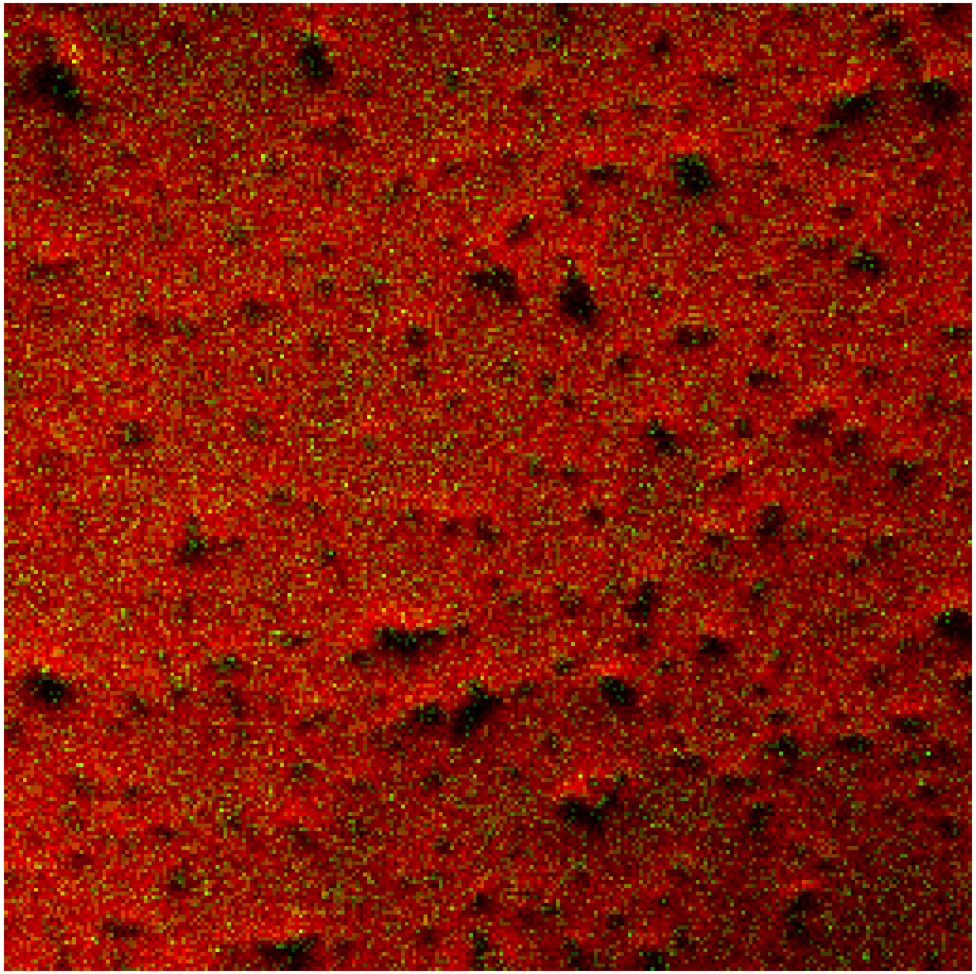
90 °C

Surface Chemical Analysis by XPS and SIMS



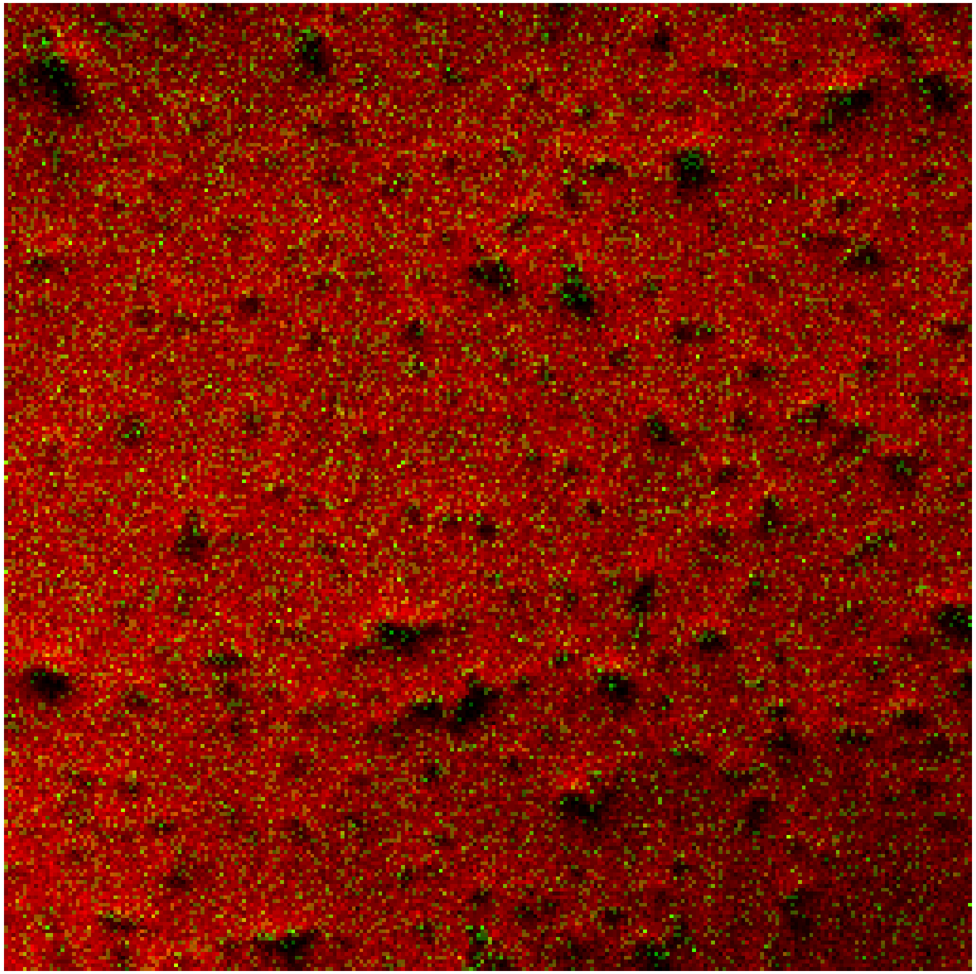
105 °C

Surface Chemical Analysis by XPS and SIMS



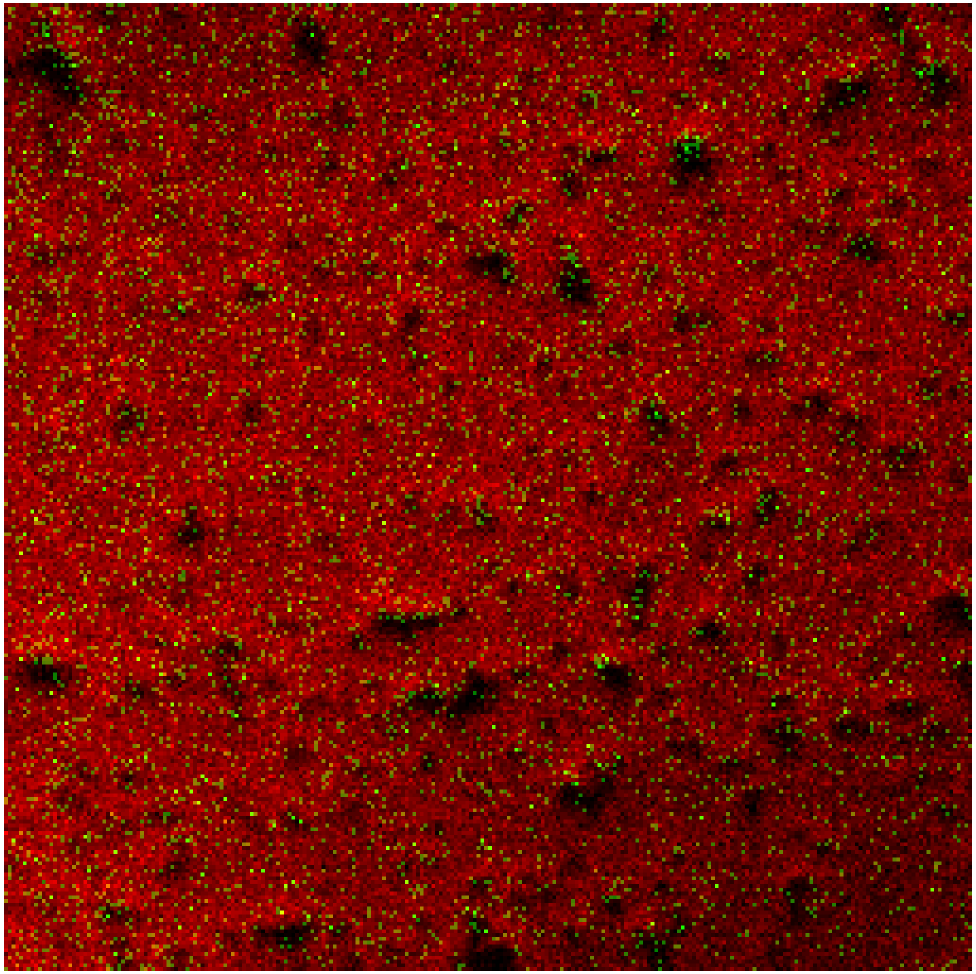
120 °C

Surface Chemical Analysis by XPS and SIMS



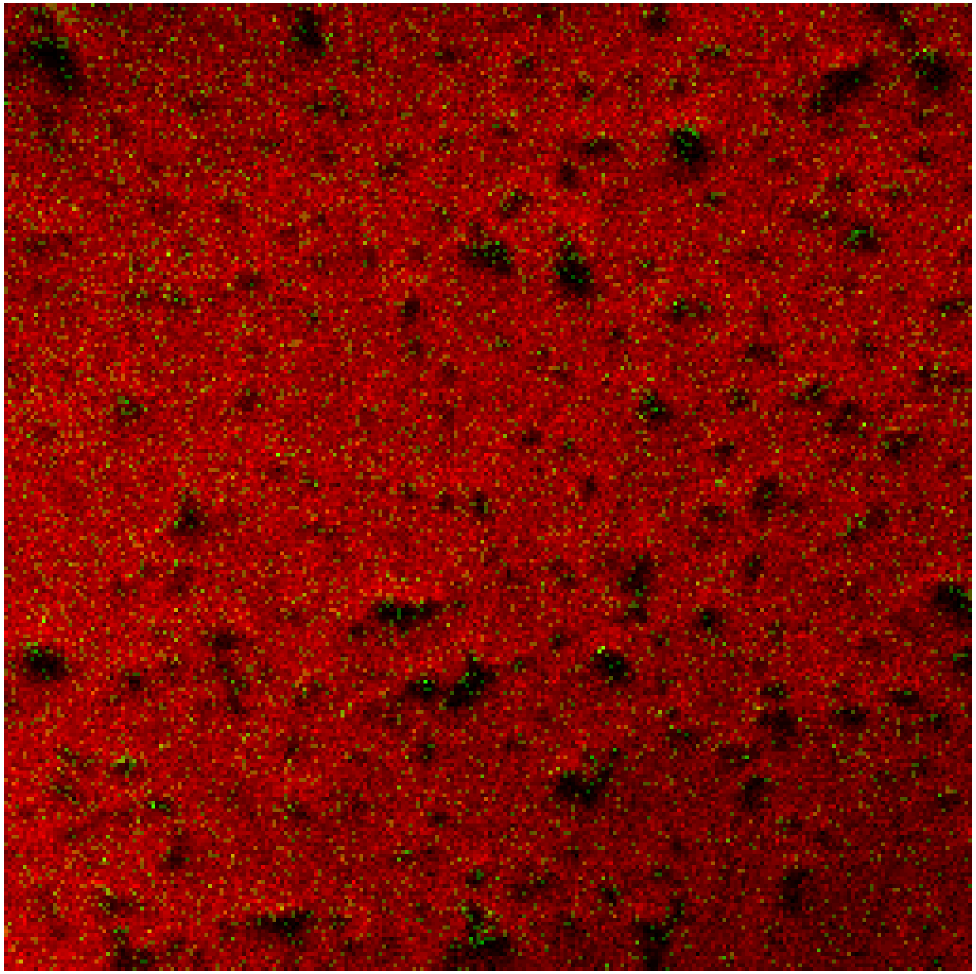
135 °C

Surface Chemical Analysis by XPS and SIMS



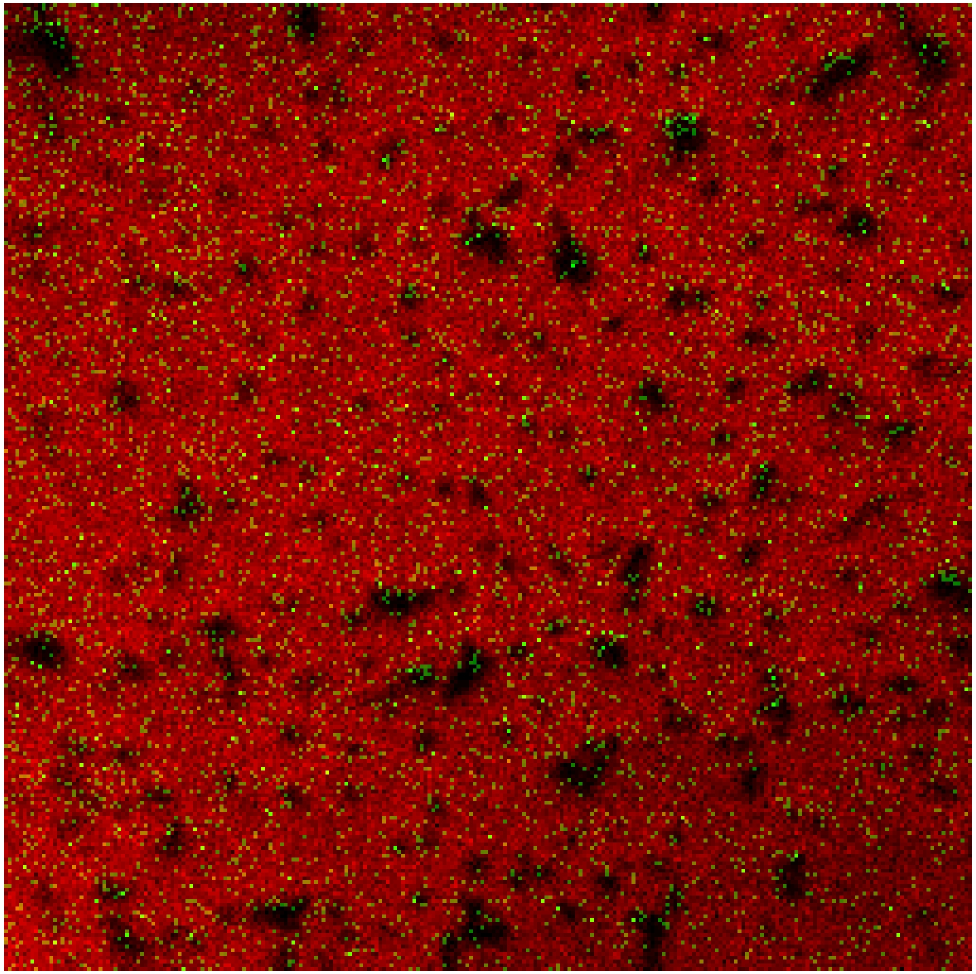
150 °C

Surface Chemical Analysis by XPS and SIMS

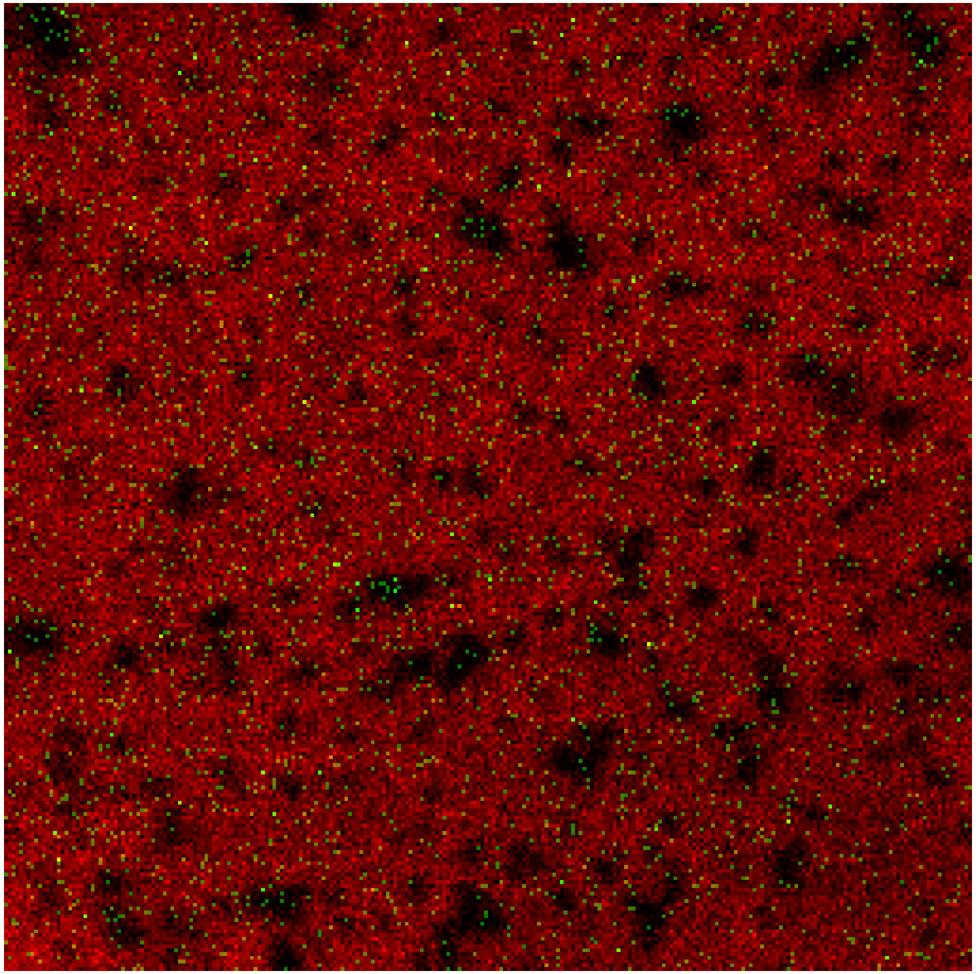


165 °C

Surface Chemical Analysis by XPS and SIMS

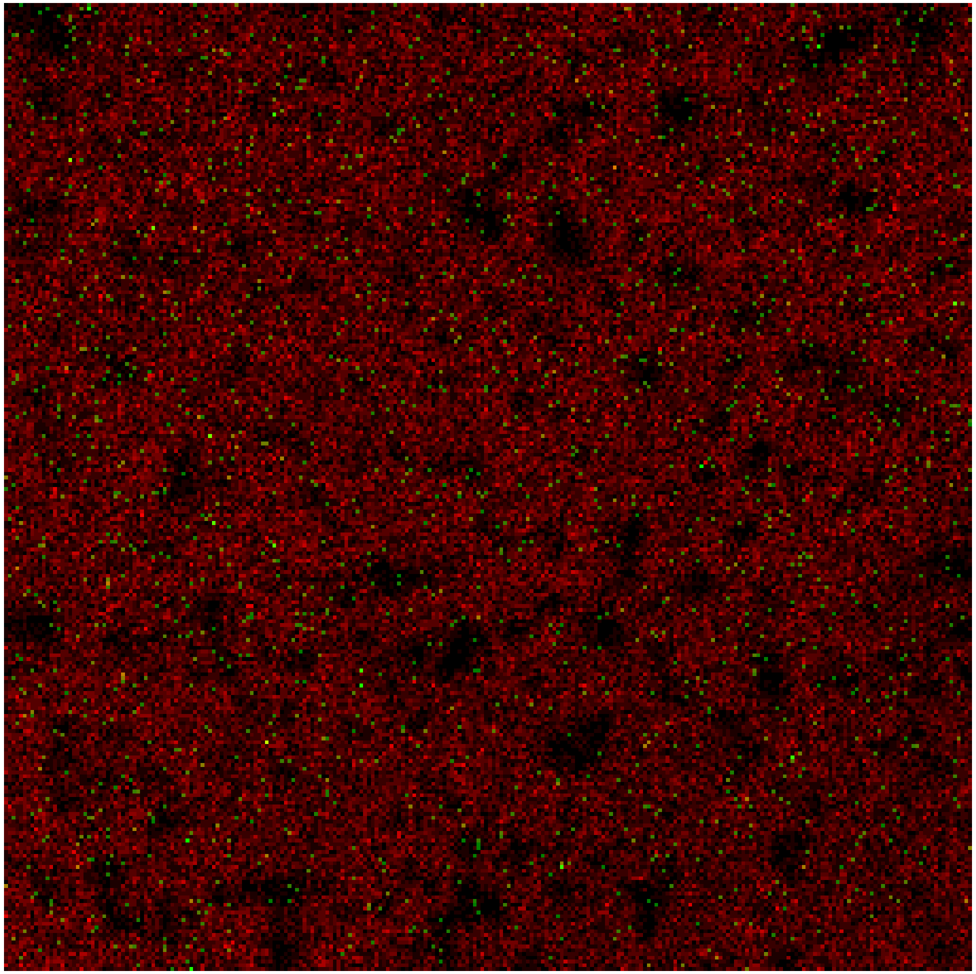


195 °C



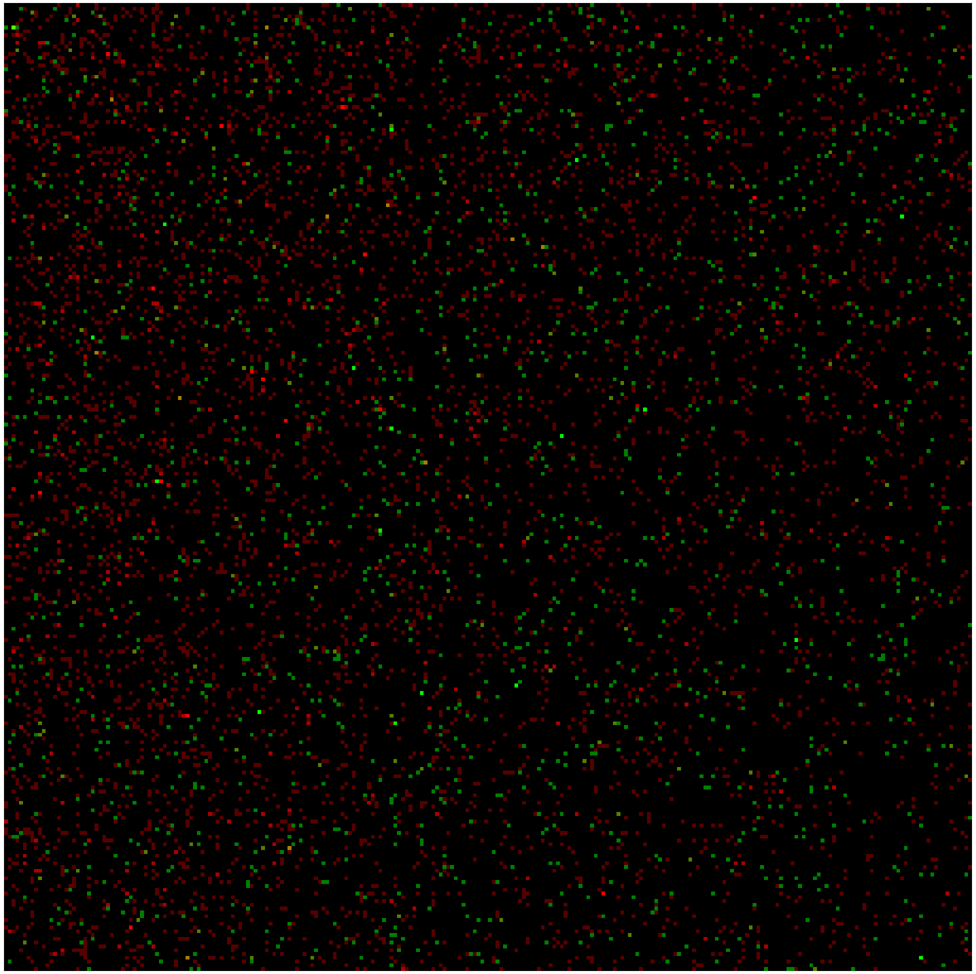
225 °C

Surface Chemical Analysis by XPS and SIMS

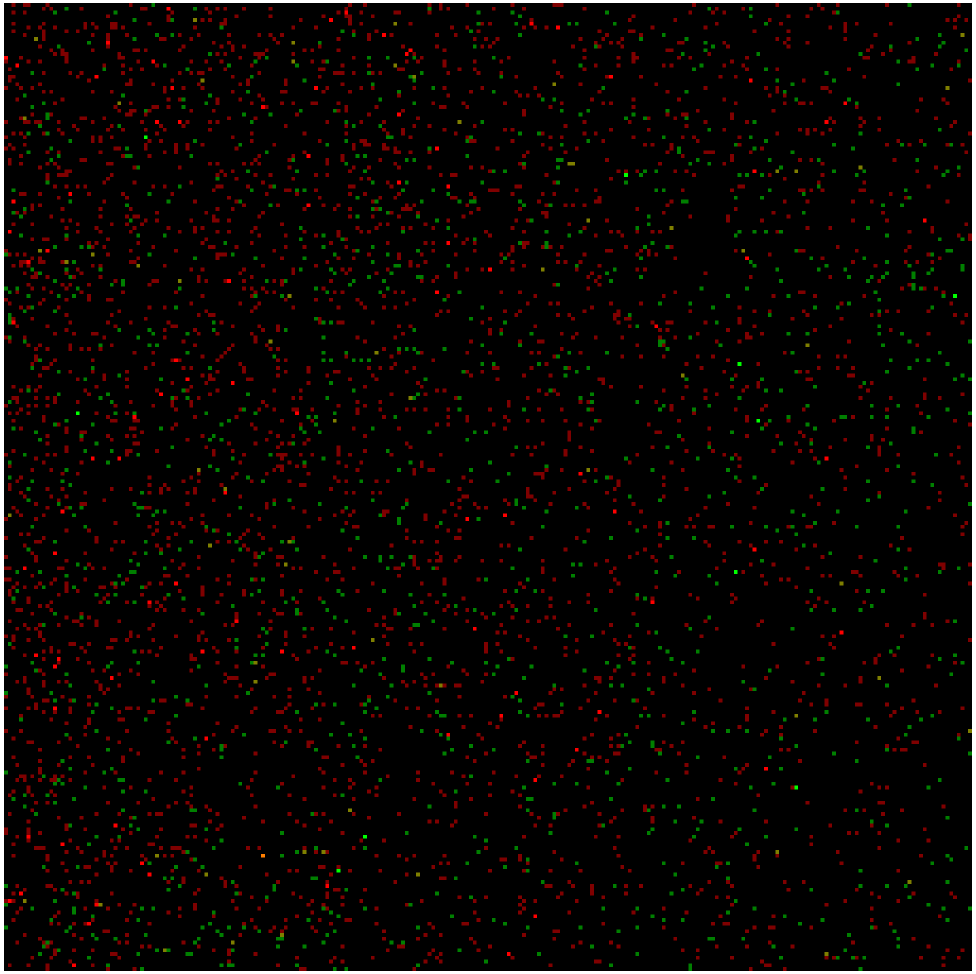


255 °C

Surface Chemical Analysis by XPS and SIMS



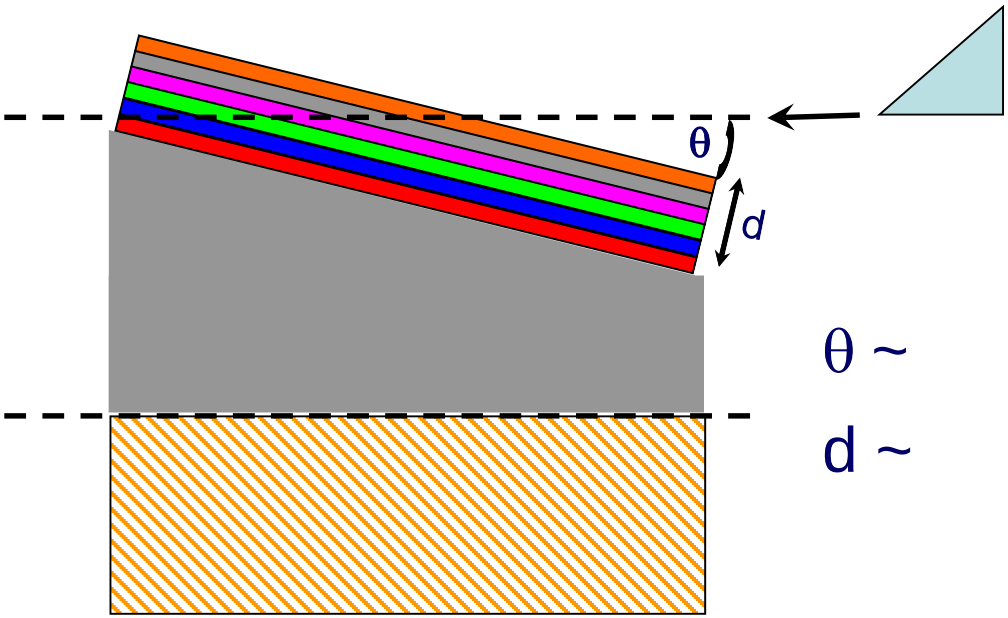
285 °C



315 °C

Buried Interfaces & Depth Profiling of Organic Materials

- Ultra Low Angle Microtomy - ULAM
    - small samples
    - glass / diamond knife
    - prepare many samples



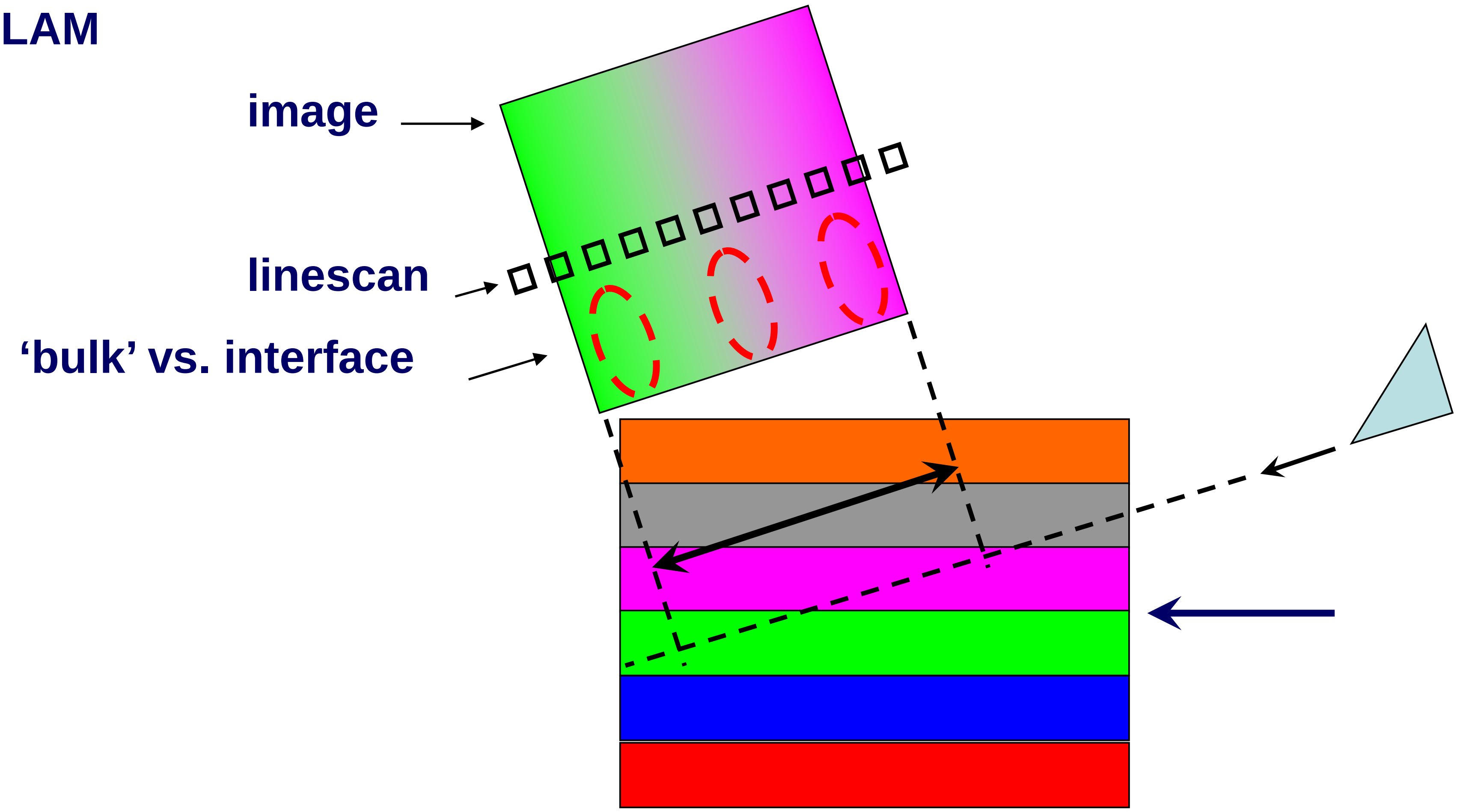
θ ~ 0.02°

d ~ 0.3 microns per mm

0.3nm per micron

Depth Profiling of Organic Materials

- ULAM

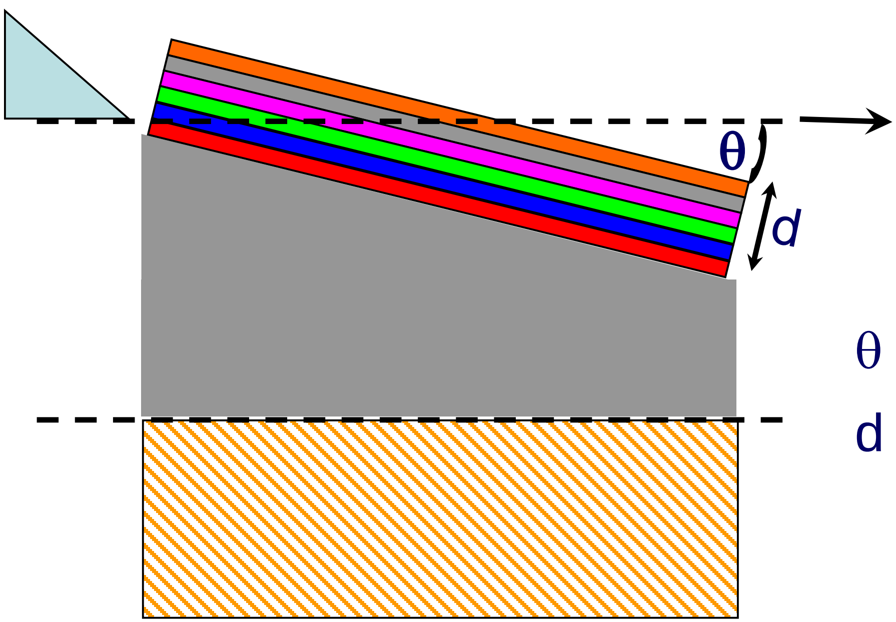


Depth Profiling of Organic Materials

- ULAM
- sampling depths
  - XPS ~ 10nm
  - SSIMS ~ 1nm
- spatial resolution / depth resolution
  - XPS ~ 55 x 55 μm = ~ 17 nm at 0.02°
  - SSIMS ~ 100 x 100 μm = ~ 30 nm
  - iSSIMS ~ 1μm = ~ 1 nm

Depth Profiling of Organic Materials

- ULAM
    - spreading of mobile species?
    - cut inside to out as well
    - cryo prep



θ ~ 0.02°

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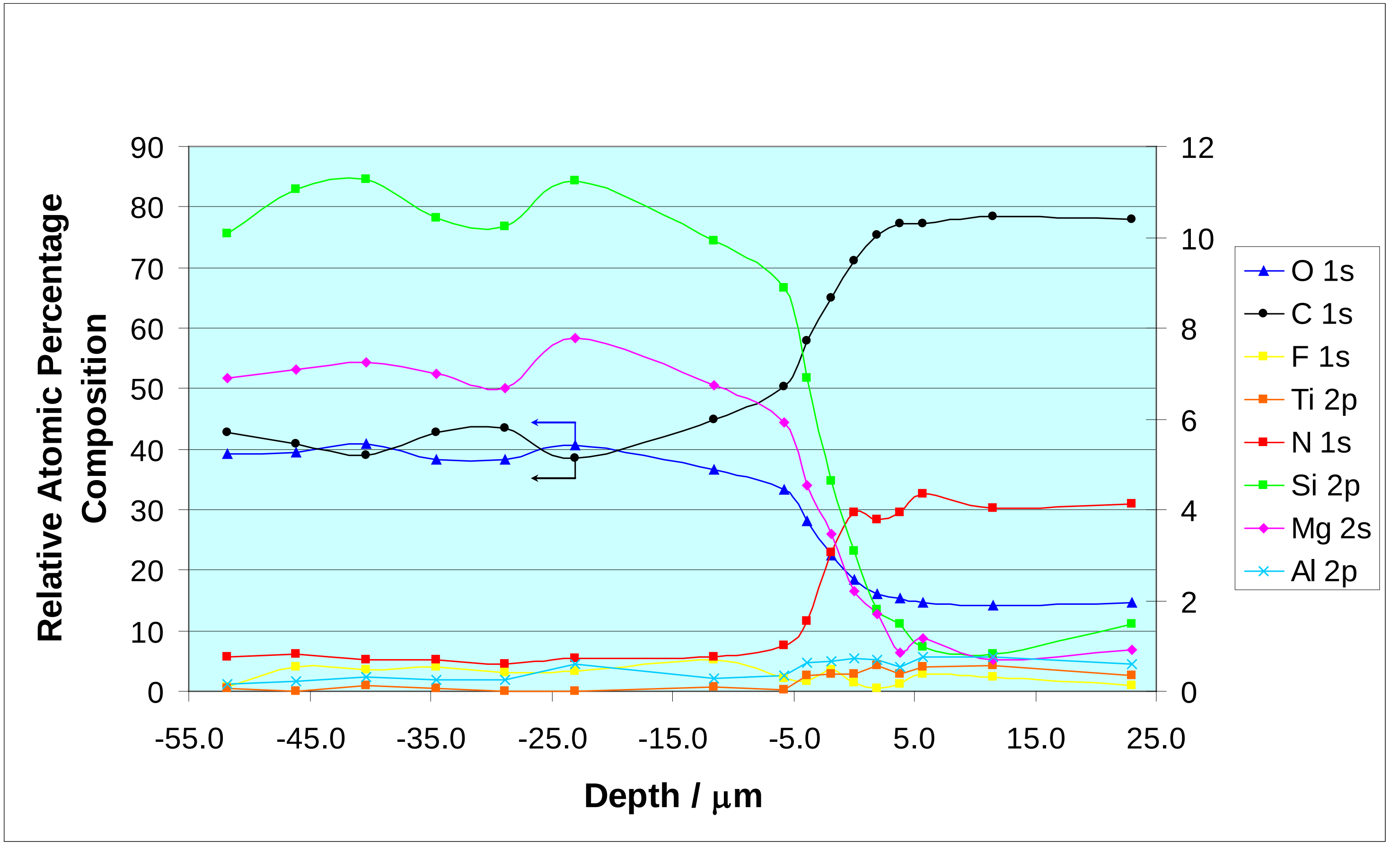
0.3nm per micron

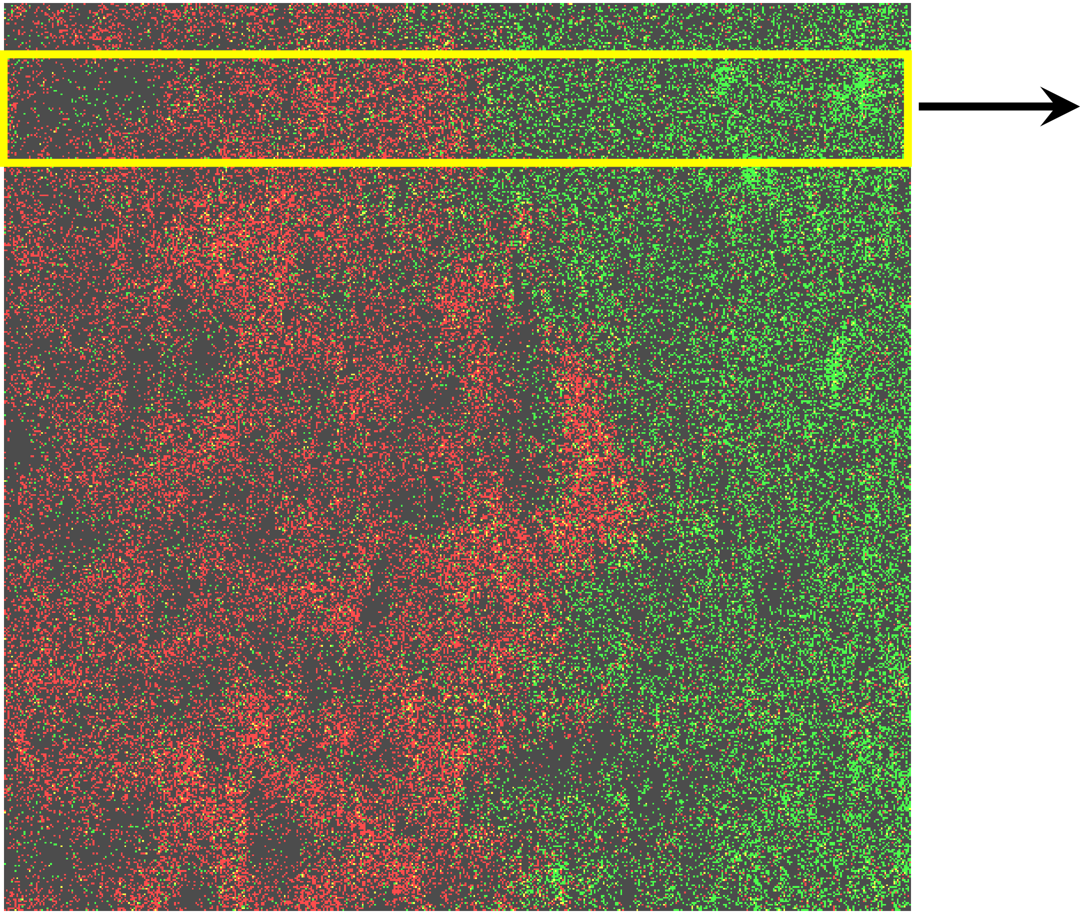
Depth Profiling of Organic Materials

- **ULAM**



Depth Profiling of Organic Materials

- ULAM



Depth Profiling of Organic Materials

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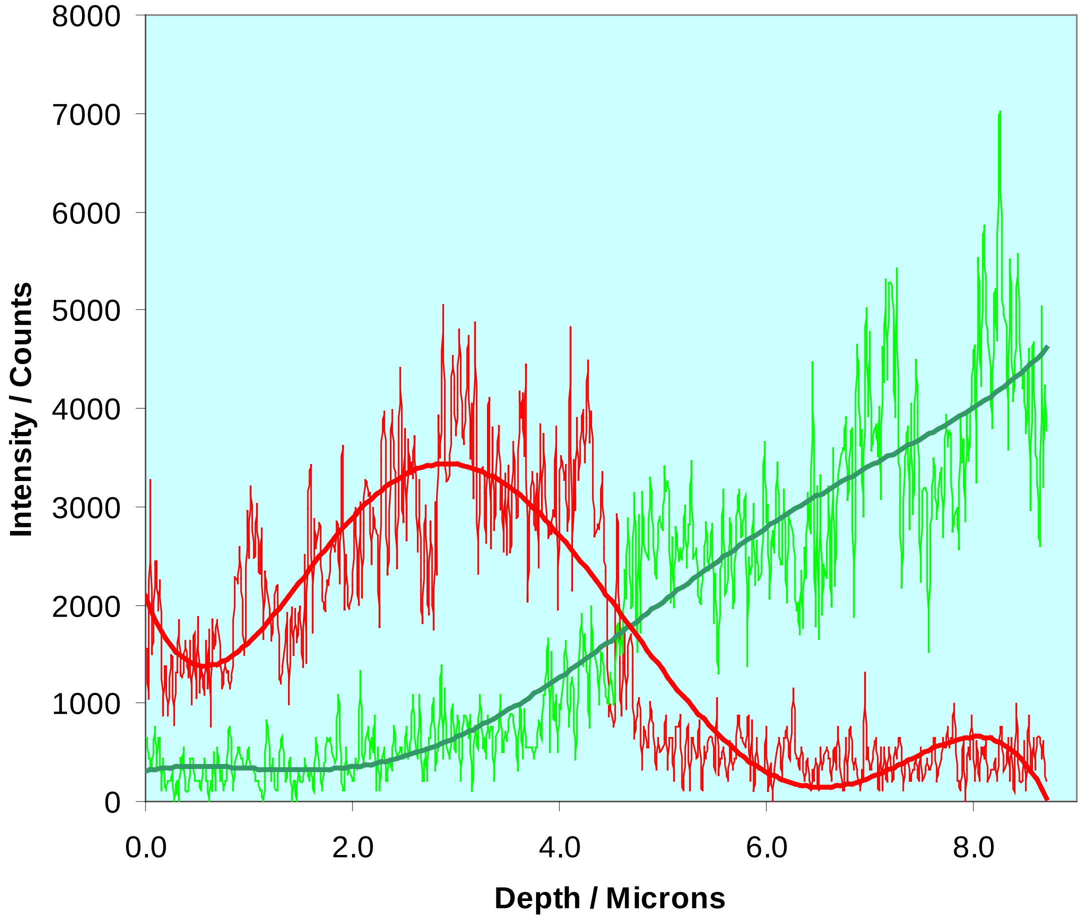

Depth Profiling of Organic Materials

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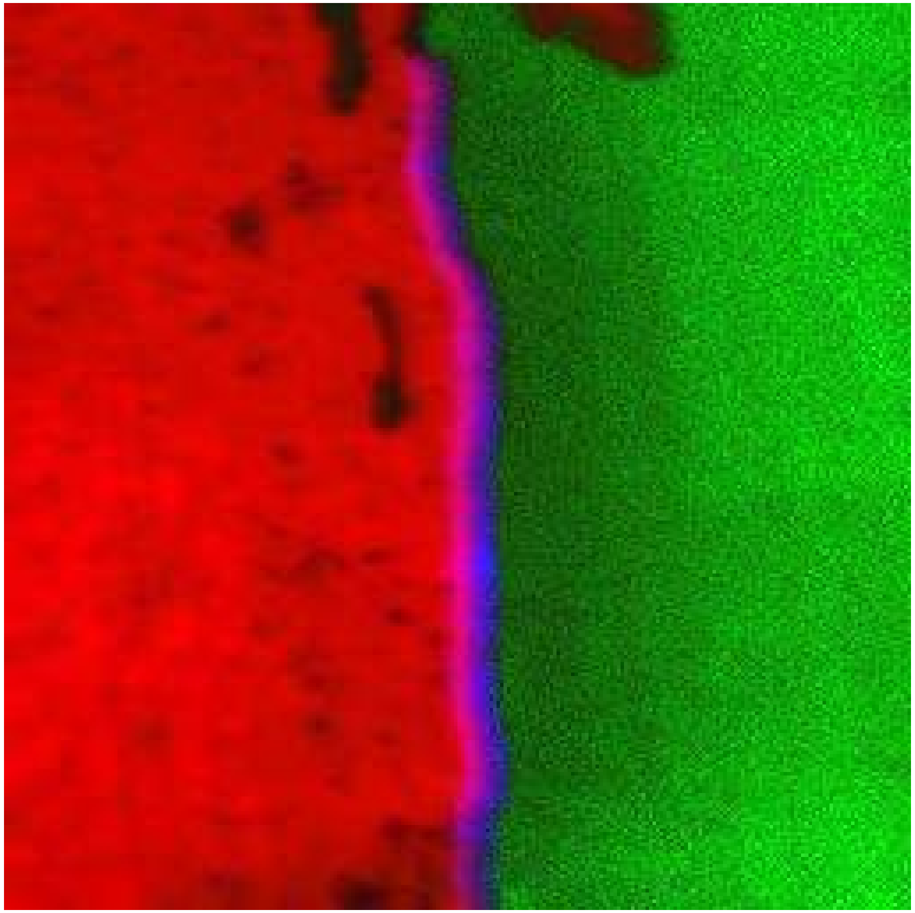
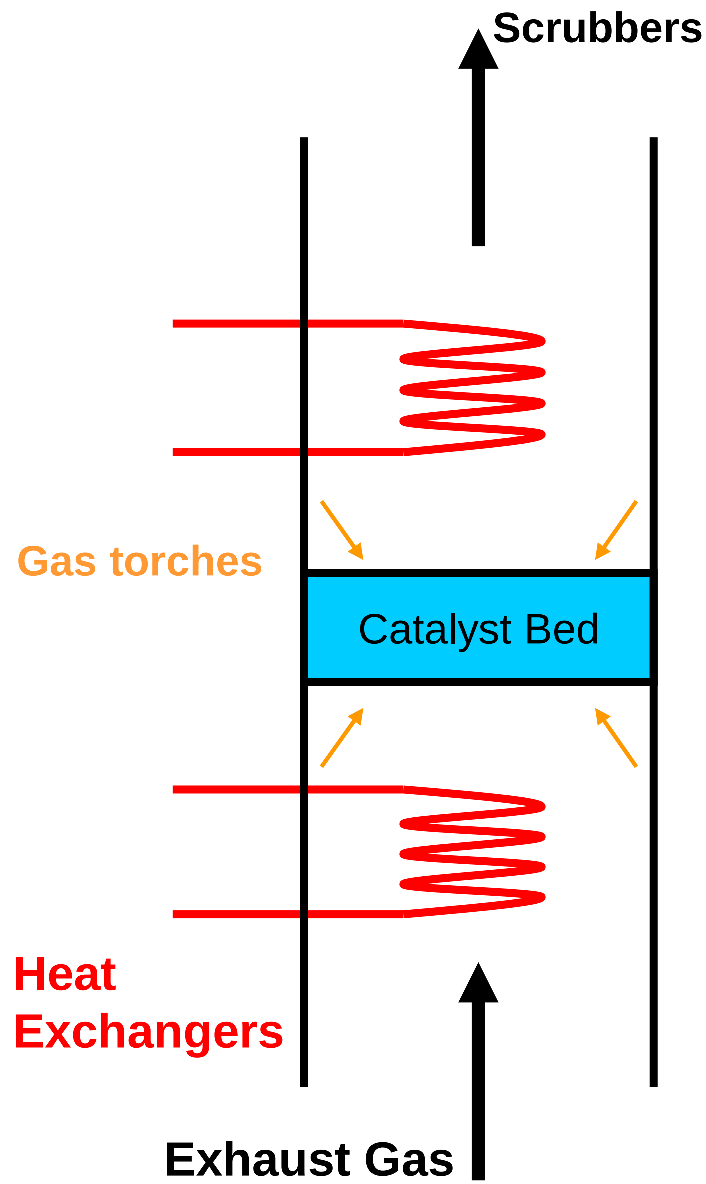


Surface Chemical Analysis by XPS and SIMS

Catalyst deactivation problem

- Problem encountered during commissioning of a new plant design



Surface Chemical Analysis by XPS and SIMS

Catalyst deactivation problem

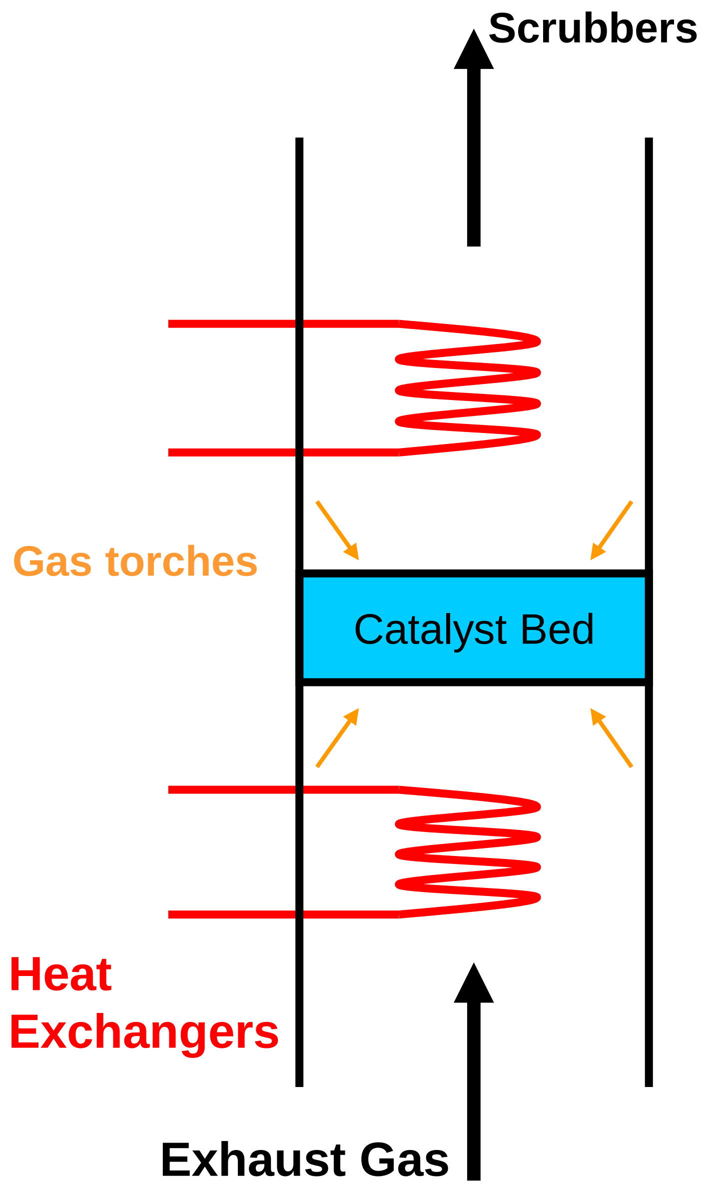
- Problem encountered during commissioning of a new plant design
- Exhaust catalyst damaged within minutes of start-up

Why?

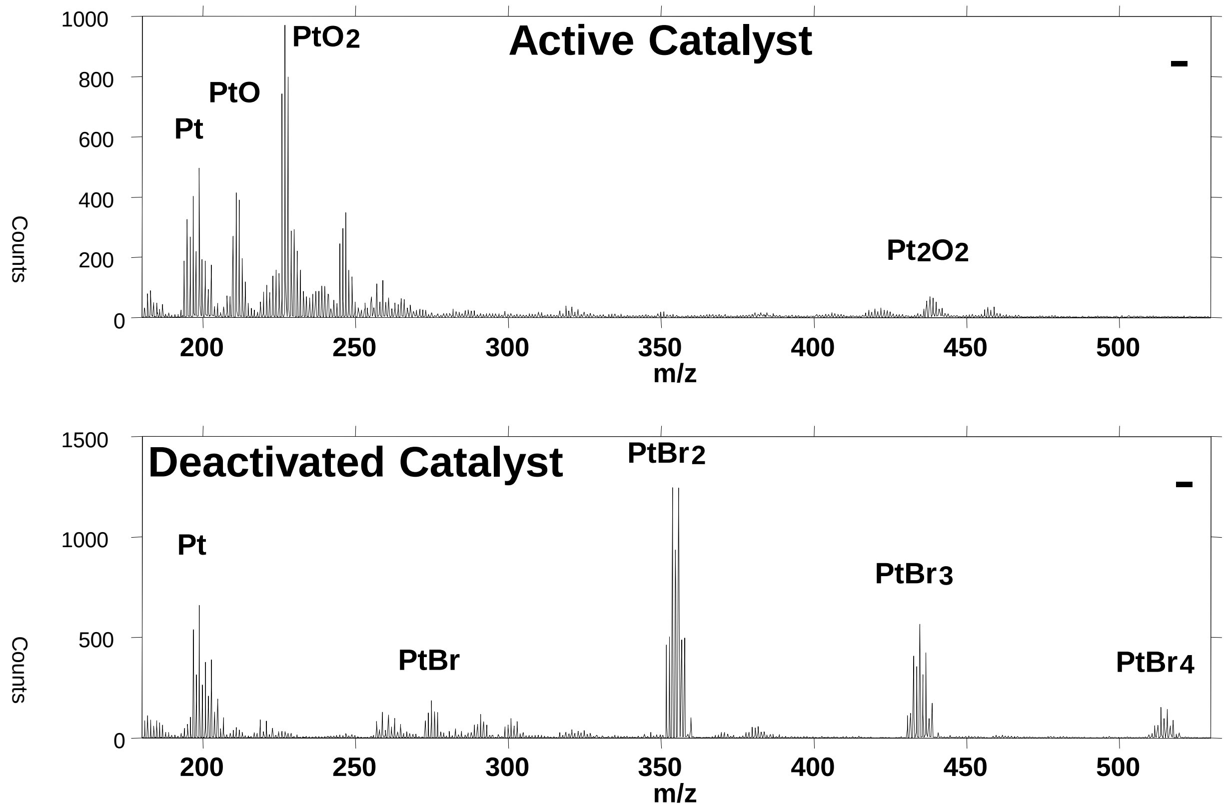
Fit a new £0.5M catalyst or not?

Urgent problem received on a Friday evening!

Initial SSIMS and XPS analysis ….



Surface Chemical Analysis by XPS and SIMS

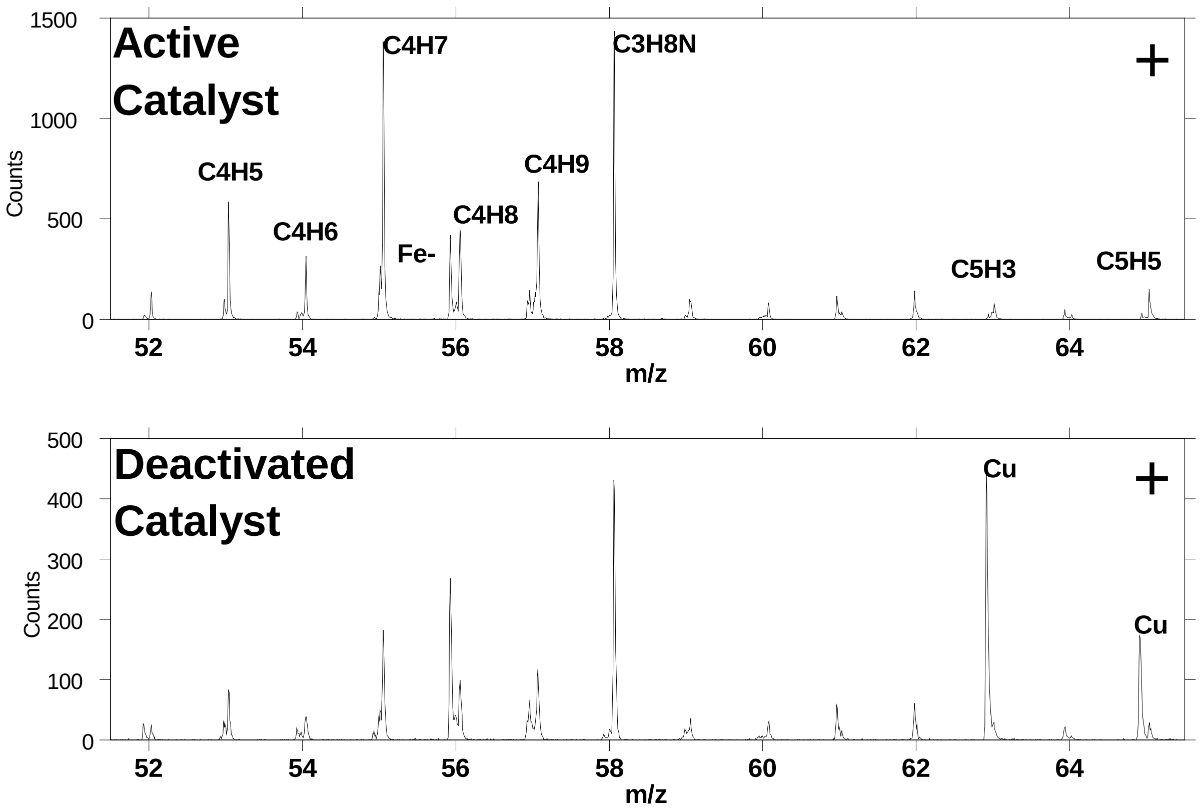


Note: Br present at ~ 5 atoms in 1000 by XPS

Bromomethane present in exhaust gas stream at low level

BUT – no reaction with catalyst under *any* conditions

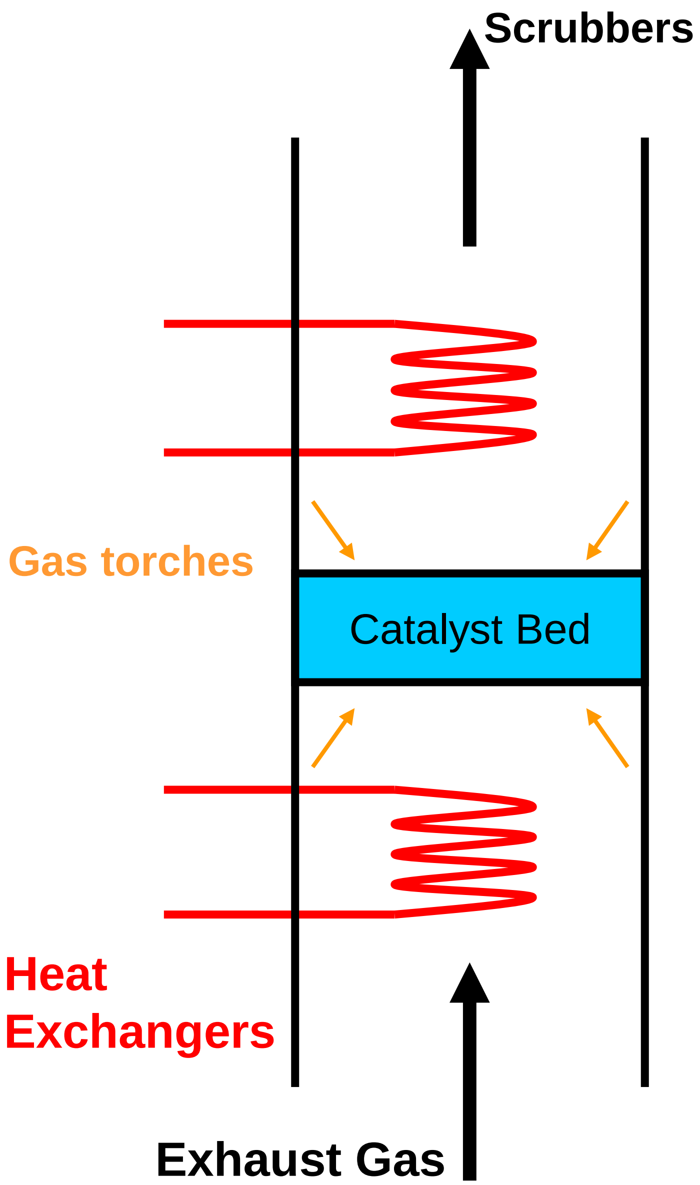
Surface Chemical Analysis by XPS and SIMS



Note: Cu present at only 1 atom in 1000 by XPS

Catalyst deactivation problem

- root cause identified
- temporary fix
- longer term solution £10M cost



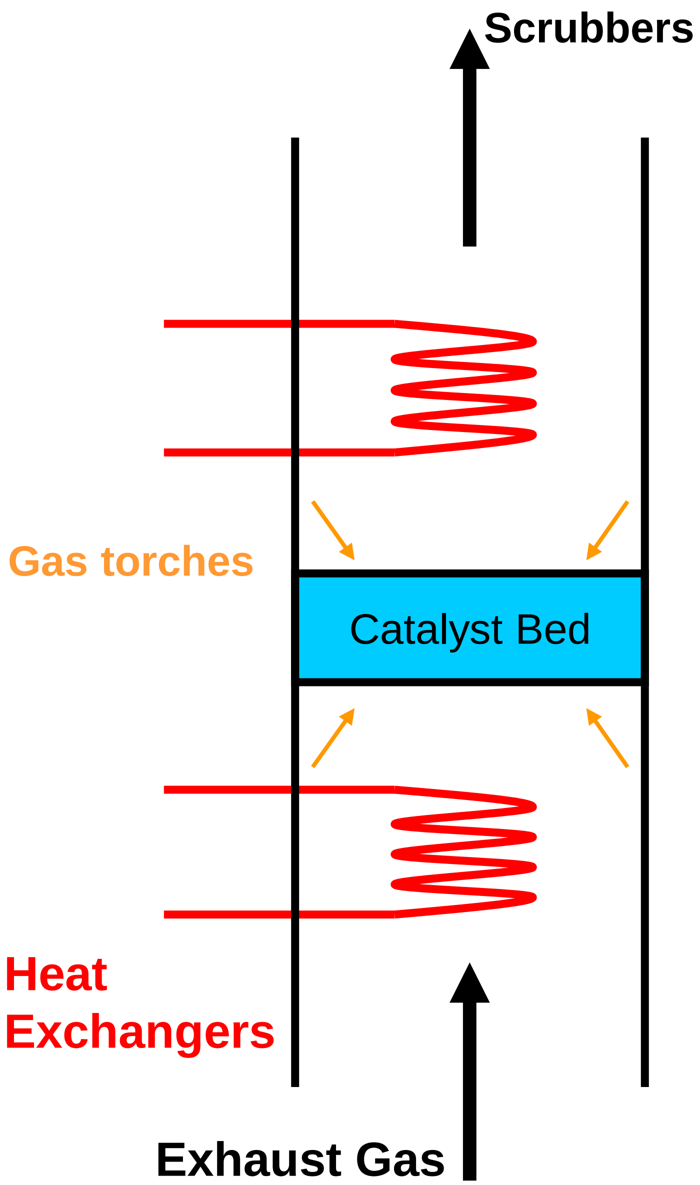
Surface Chemical Analysis by XPS and SIMS

Catalyst deactivation problem

- root cause identified
- temporary fix
- longer term solution £10M cost

- saved £0.5M catalyst
- license to operate £200M investment
- reputation

- 2 similar plant designs …



Conclusions

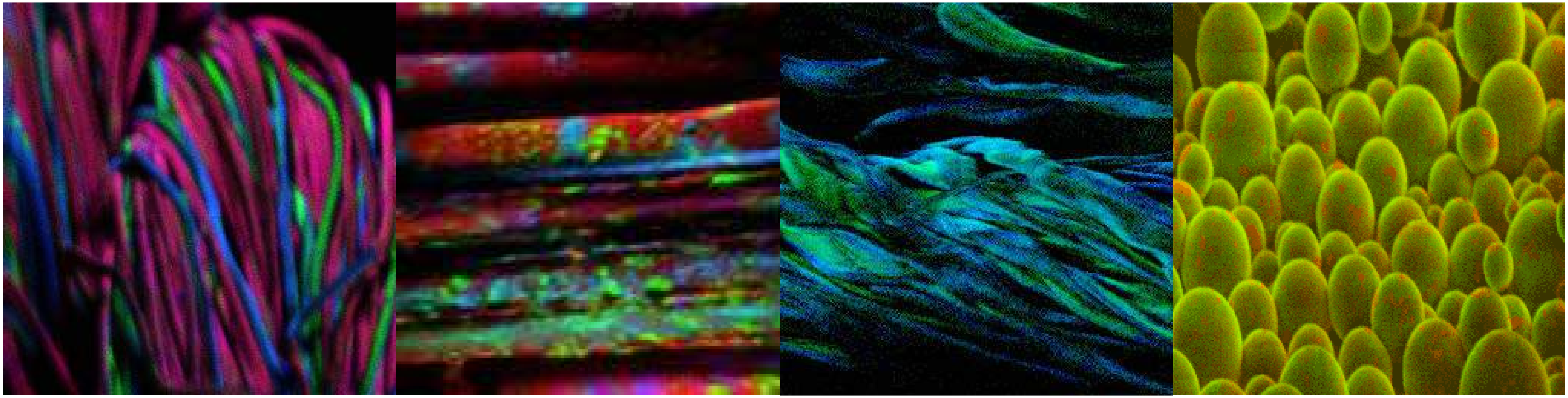
- **XPS and SIMS should be considered whenever surface chemistry is involved or when surface chemical information is required**
- **Very powerful capabilities at SEAL – available to all!**
- **Capability = f {equipment, people (experience + ability)}**
- **Enabling support for research and development**
- **Problem solving support for processes and production**
- **Pushing the limits**

Conclusions

- XPS and SIMS should be considered whenever surface chemistry is involved or when surface chemical information is required
- Very powerful capabilities at SEAL – available to all!
- Capability = f{equipment, people (experience + ability)}
- Enabling support for research and development
- Problem solving support for processes and production
- Pushing the limits
- If you have a problem, if no one else can help, and if you can find them, maybe you can hire ... the SEAL Team!

Conclusions

- SEAL has the best instrument base for surface analysis in Europe including XPS, ToFSIMS, Gas Cluster Ion Beams and Helium Ion Microscopy facilities
- Also UPS, ISS, SEM, EDX, FIB, AES, AFM, SPM, QCM, GDOES, White-Light Interferometry and Raman Microscopy
- If we can't do it, it probably can't be done!



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- Thank you for the invitation and for your attention!