2 September 2016

THE SCIENCE OF HAIR CARE - A GOOD HAIR DAY

The Use of Surface Analysis Techniques in Hair Product Development

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LUCIDEON

Why surfaces are important?

- The surface controls factors such as:
  - Cleanliness
  - Biocompatibility
  - Adhesion strength
  - Wear performance
  - Wetting
  - Corrosion resistance
  - Optical properties e.g. colour/finish/shine
  - Electrical properties
  - Printability/paintability
  - . . . and many others

Problem solving on surfaces

- Surface analysis techniques measure the chemical and physical composition of the outermost atomic layers of a material

Chemical Composition

Secondary Ion Mass Spectrometry (SIMS)

X-Ray Photoelectron Spectroscopy (XPS)

Physical Characteristics

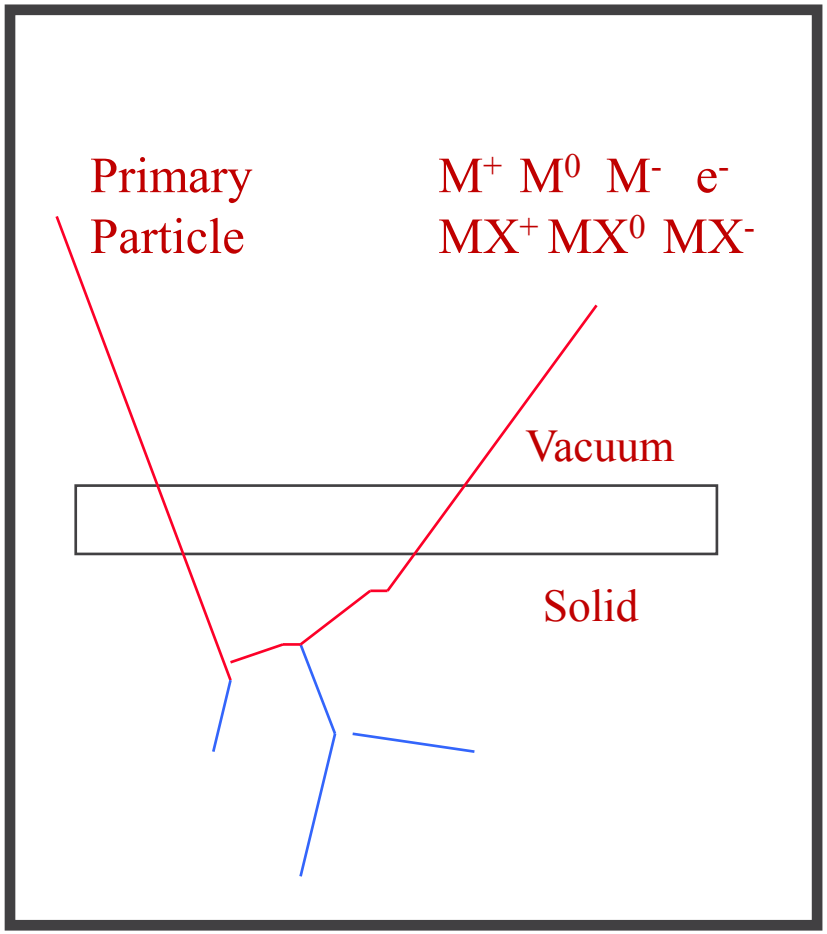
Optical microscopy

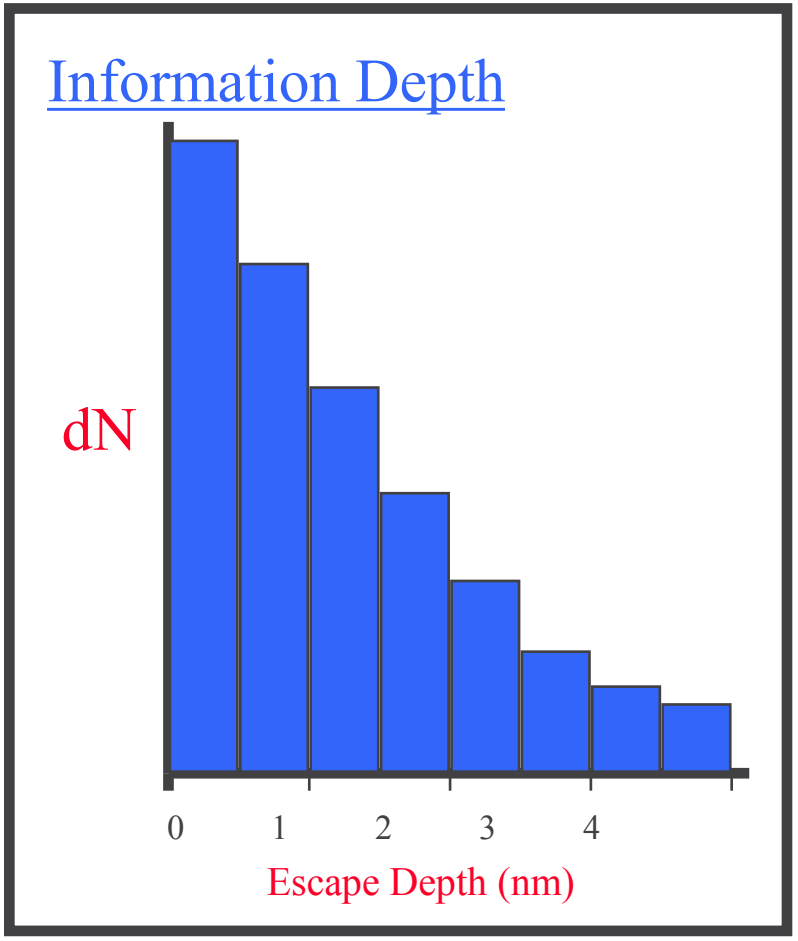
Scanning Electron Microscopy (SEM)

Surface Metrology - 3D profiling

- White light interferometry
- AFM - Atomic Force Microscopy
- 3DSEM
- Stylus Profilometry (2D)

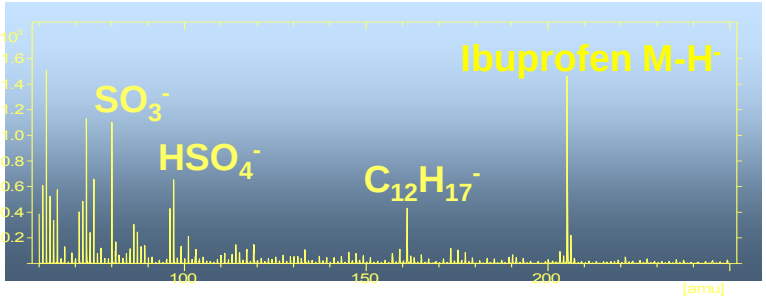
Secondary Ion Mass Spectrometry (SIMS)

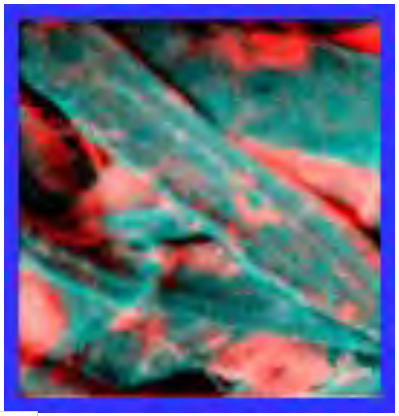


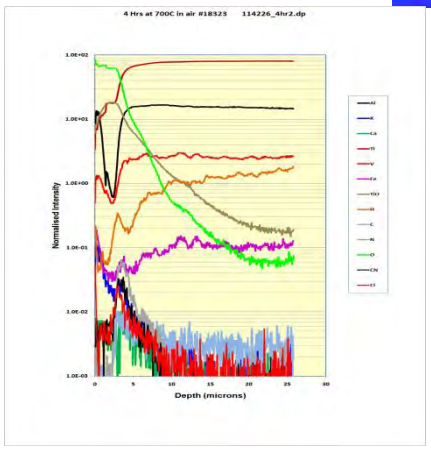


SIMS modes and data output

- Static SIMS
  - Minimal surface disruption
  - Fingerprint spectrum
- Dynamic SIMS
  - High etching rate
  - Depth profiling
- Imaging SIMS
  - Elemental and molecular mapping
  - Distribution of species







Dynamic SIMS vs static SIMS

- DSIMS

Final state of surface

Elemental information
Depth profiling
Quantification
Bulk analysis ~10-30µm

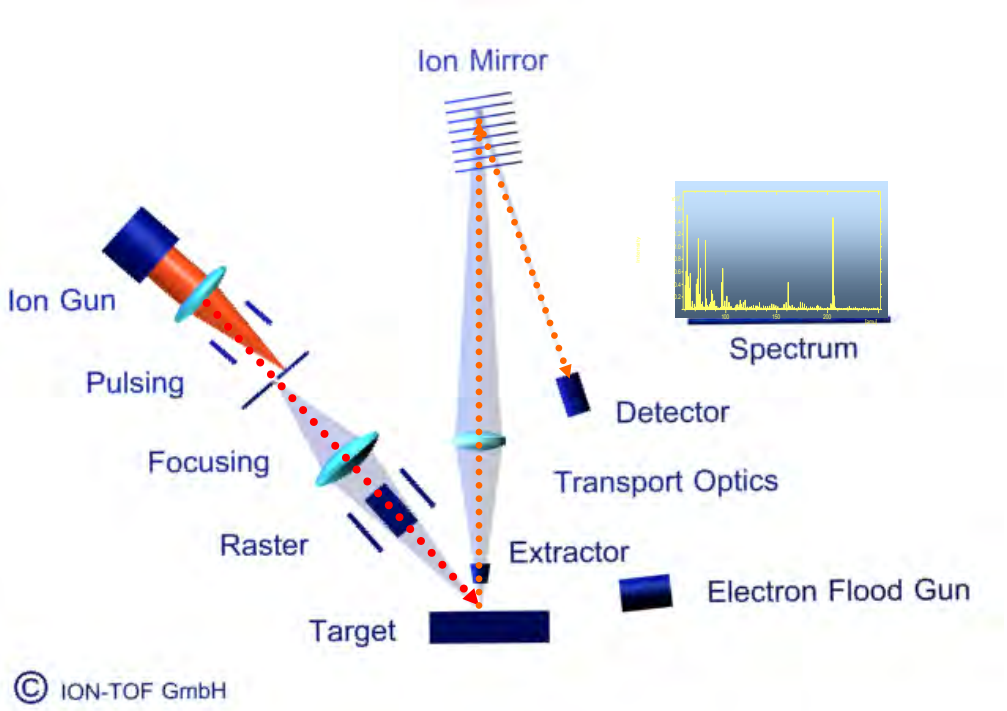
- SSIMS

Elemental + molecular information
Qualitative/semi-quantitative
Surface analysis ~1-2nm

- In SSIMS, the chemical integrity of the surface is preserved during analysis
- Each primary impact affects a pristine area

Atomic surface density ~10^{15} at.cm^{-2}
Static limit ~10^{12} ions.cm^{-2}

Time-of-Flight SIMS

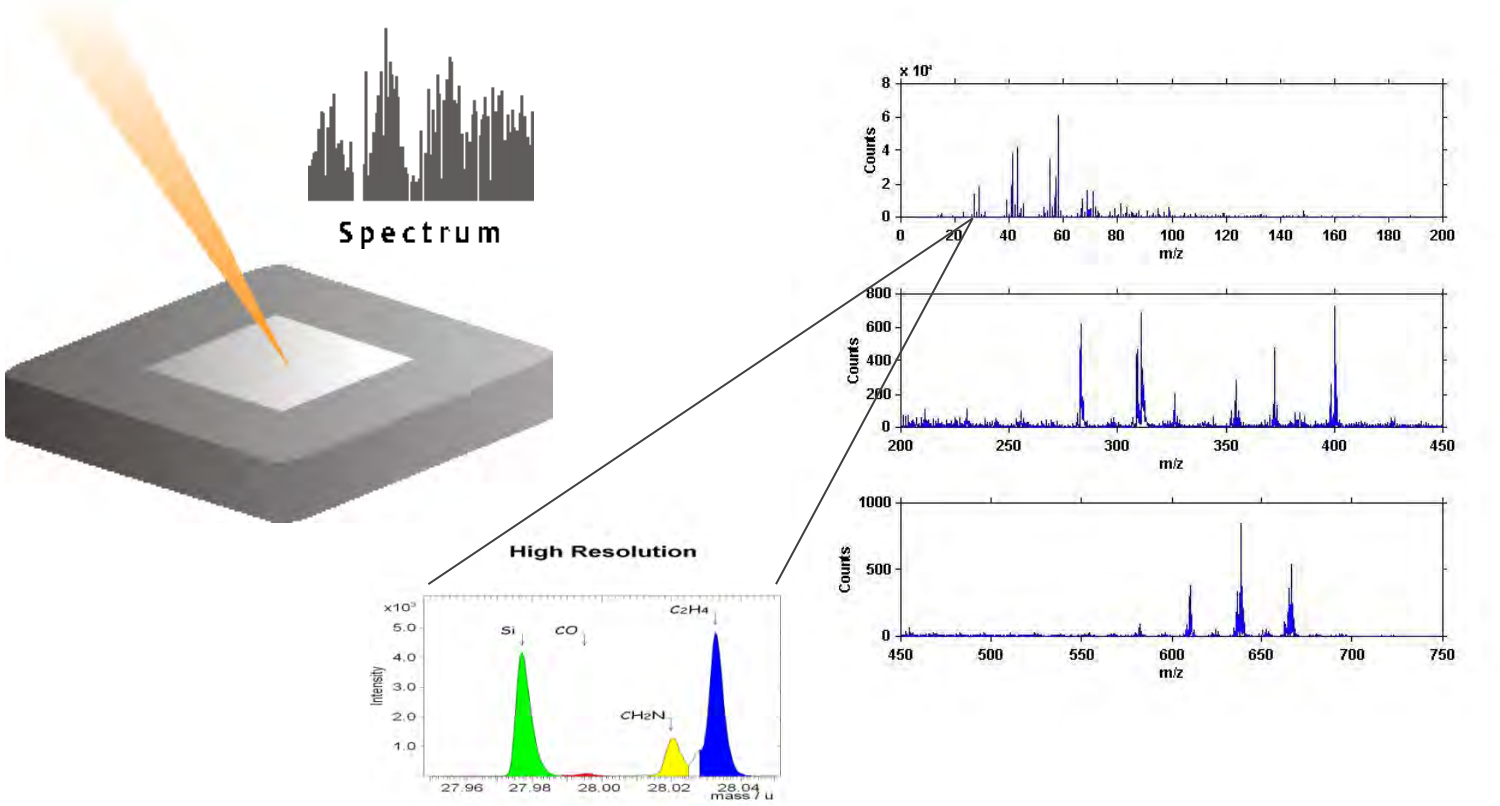


- High sensitivity
  Parallel mass detection
- High mass resolution
  Accurate Mass analysis
- Mass accuracy
  1 - 10 ppm
- Mass range
  Up to 10000 amu

Mass discrimination: the flight time of an ion varies as the square root of its mass

ToFSIMS - a mass spectrometry

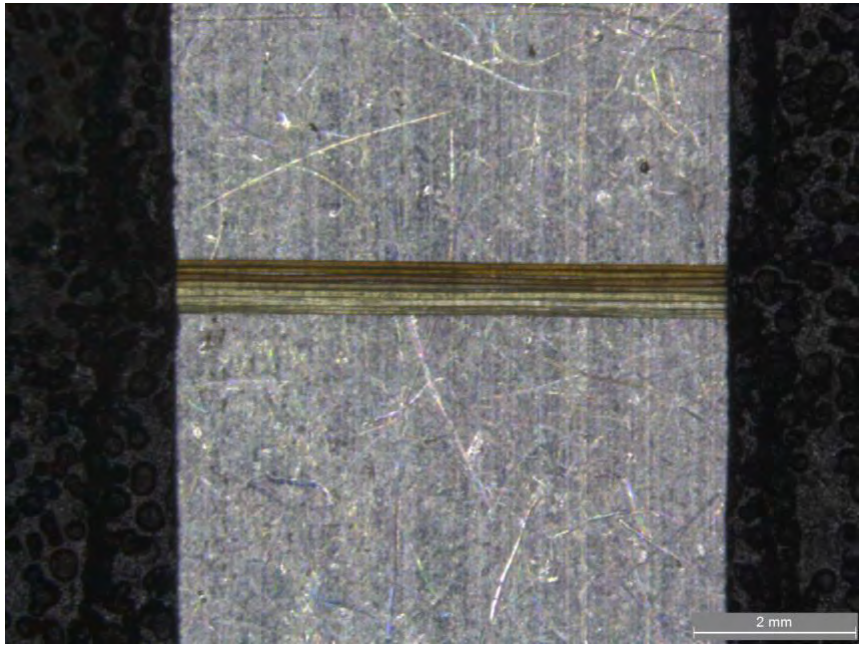
Detailed chemical and molecular structure information



Hair analysis

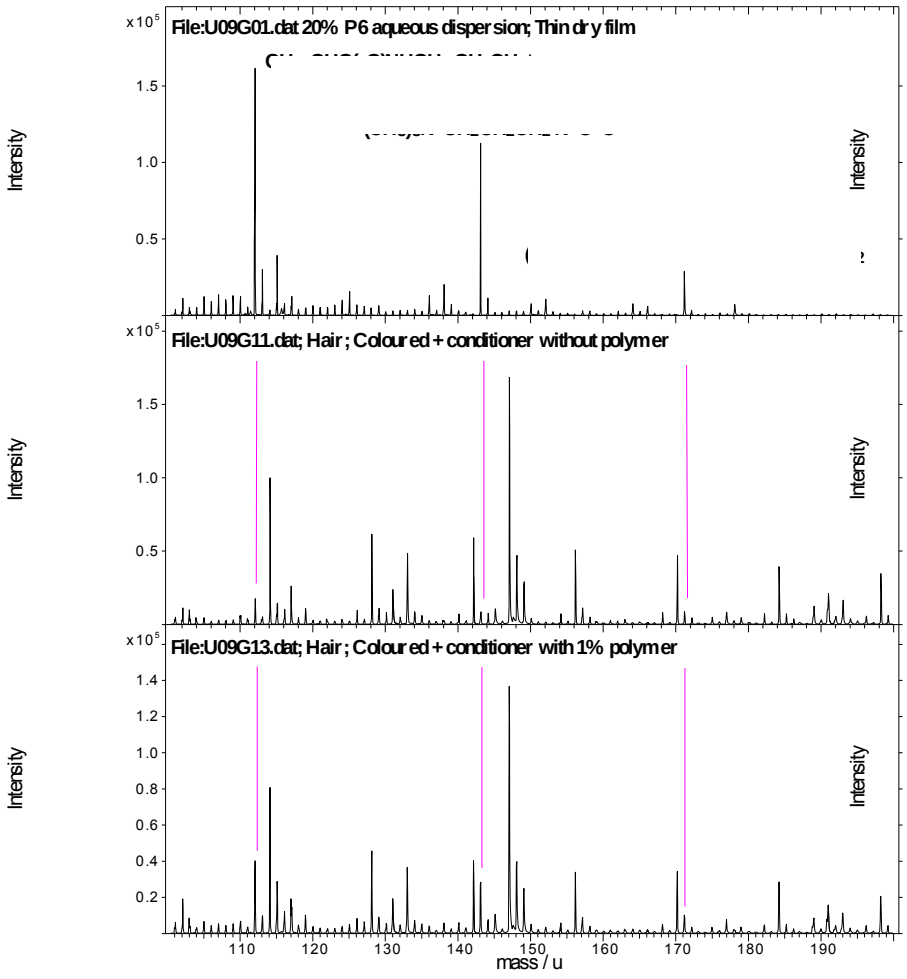
- Fibres are generally difficult to analyse due to the curvature

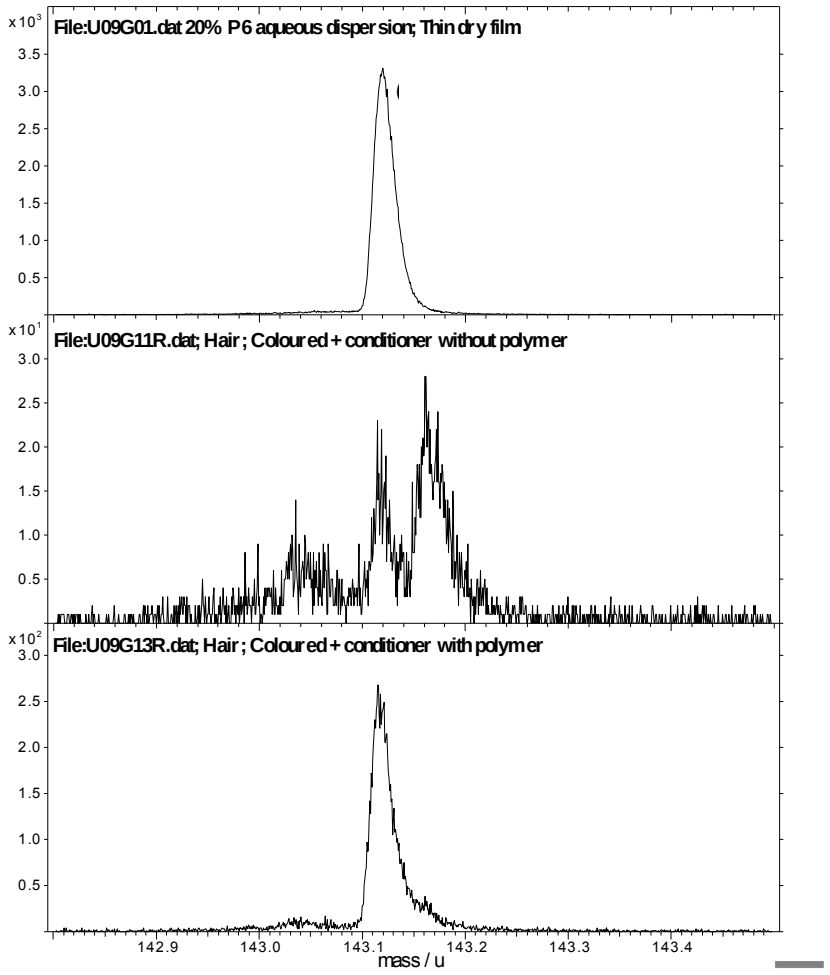
- Mounting is a critical factor affecting the quality of images
  - Individual fibres mounted parallel against each other to form a “flat bed” and present a more uniform surface to minimise distortions due to field effects in the images



Identification of an active on conditioned hair

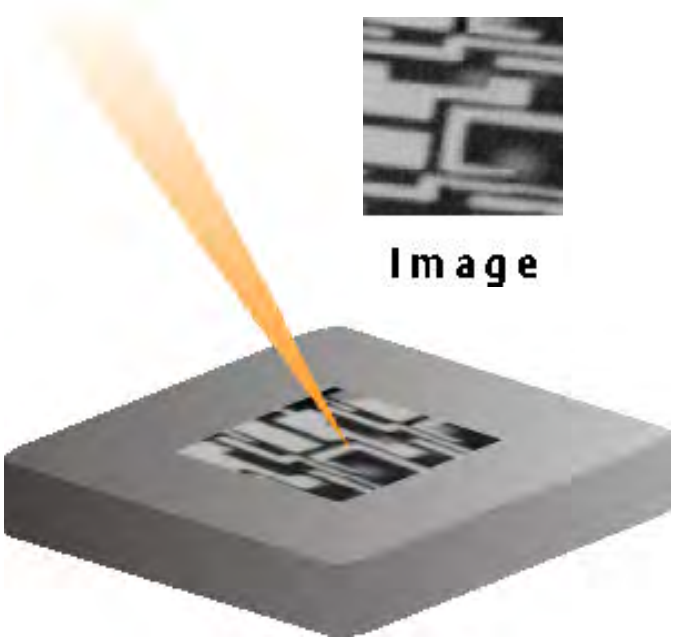
Active: polymeric quaternary amino chloride





ToFSIMS imaging

- Spatial distribution of species on the surface



Focused pulsed ion beam rastered over the surface

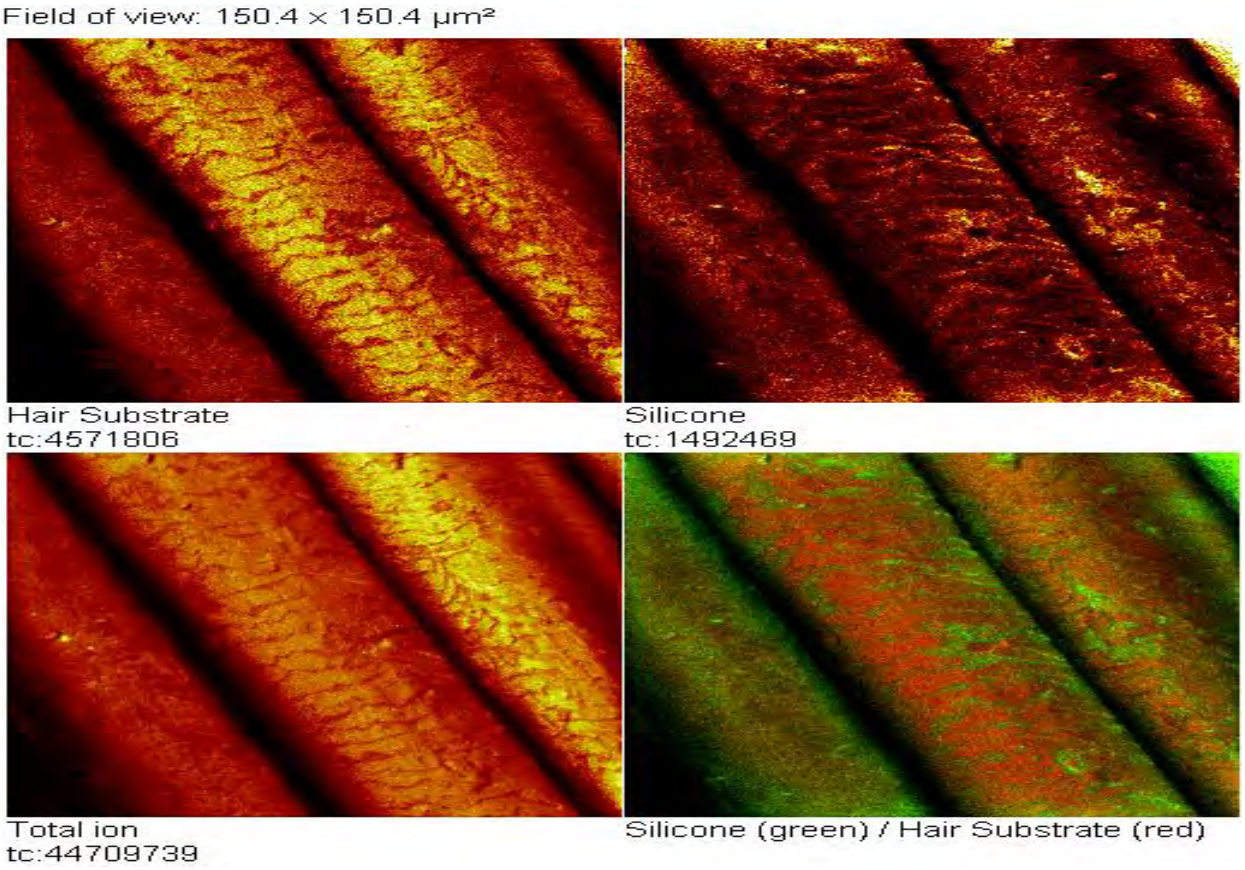
X, Y coordinates recorded with flight time of ions to produce mass resolved secondary ion images

Chemical mapping with sub-micron lateral resolution: < 200nm at best

Typically used for areas < 150µm; larger areas (up to 500µm) ~3 - 5µm resolution used

- Retrospective analysis
- Spectrum-per-point (raw data) analysis
- Region-of-Interest reconstruction

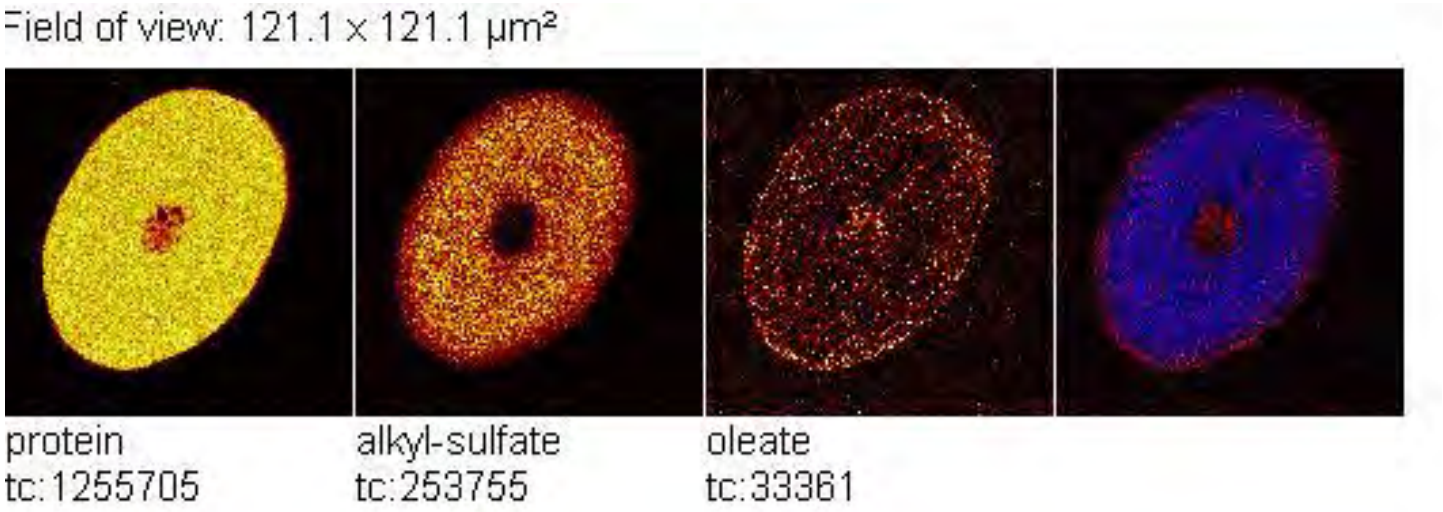
Silicone-containing shampoo on bleached hair



Silicone deposition is clearly identified and the signal intensity indicates how much silicone is present

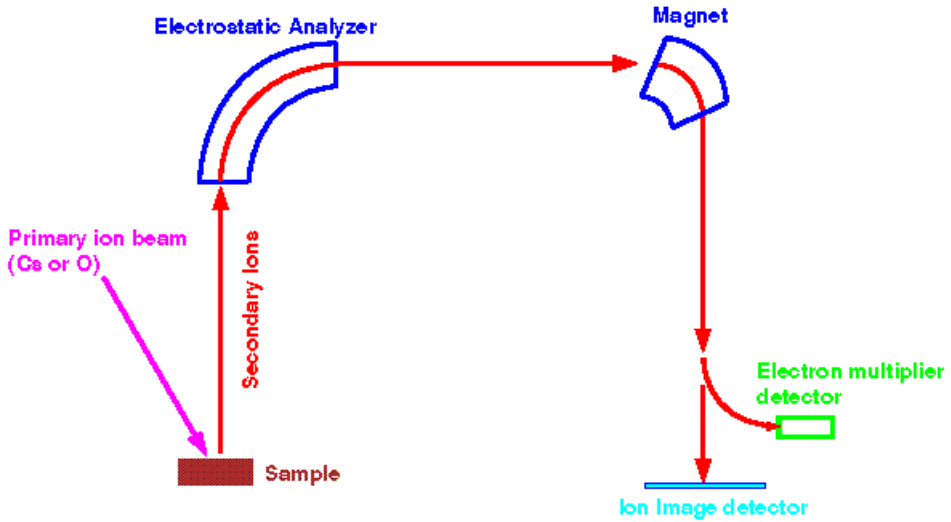
Hair section

- Microtoming of hair embedded in resin
- Determination of penetration of species into the hair shaft



DSIMS

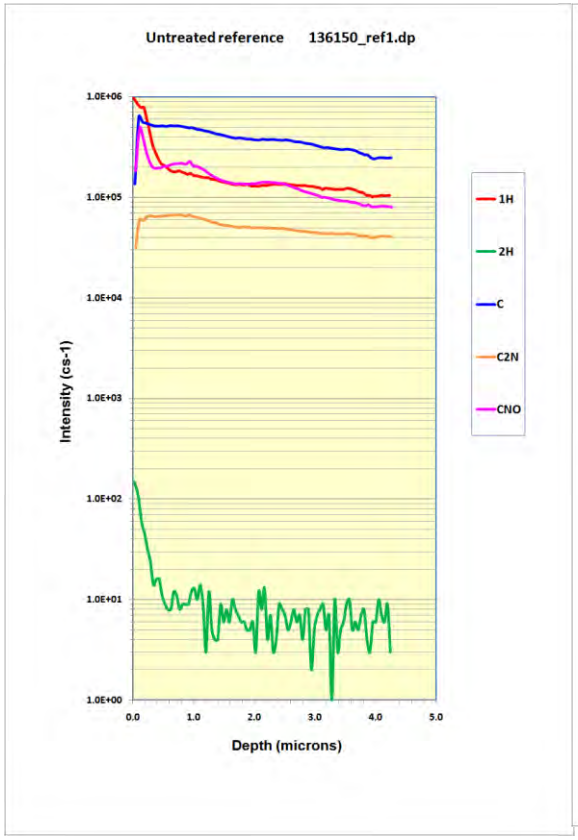
- Forces of electric field and magnetic field used for mass discrimination
- Scanned instrument
  - Higher primary ion doses hence more destructive and less suitable for organic materials
  - Elemental information mainly

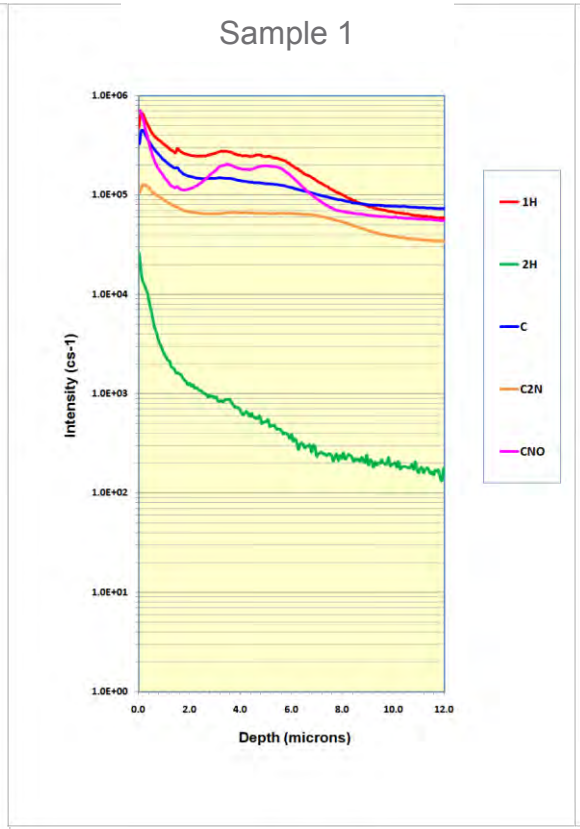


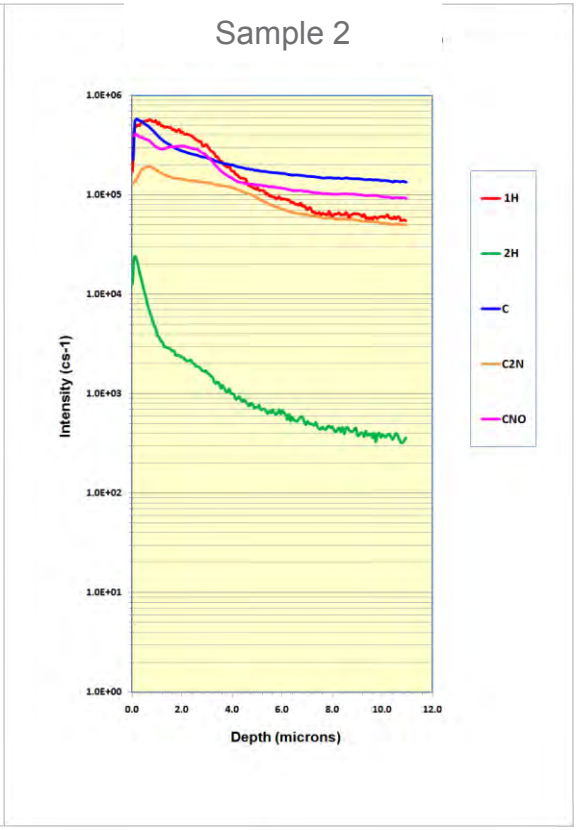
Depth profiling

Deuteration of small active molecules used in hair treatment

^{2}H signal used to monitor penetration of species



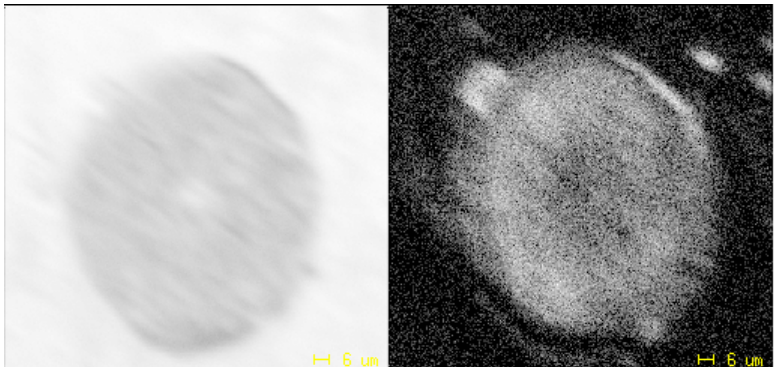


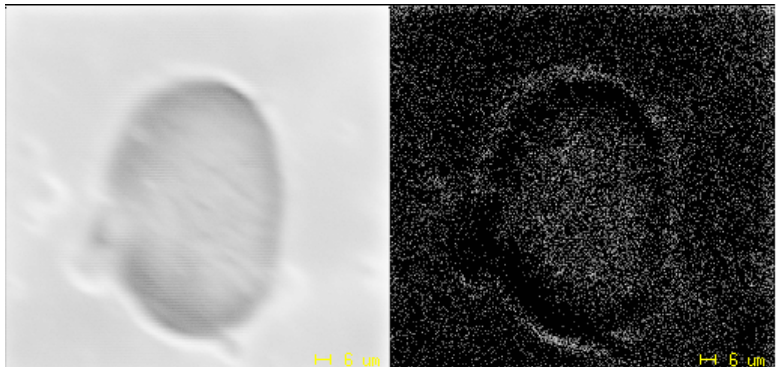


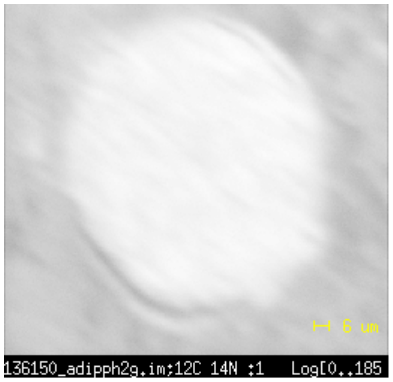
Untreated

Penetration deeper than 12 microns

Hair section - imaging



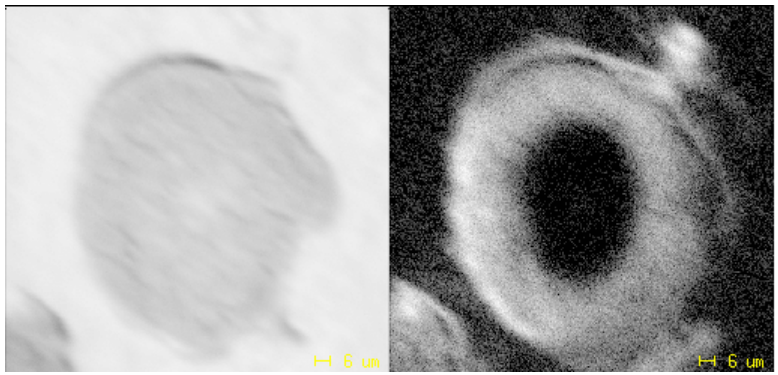


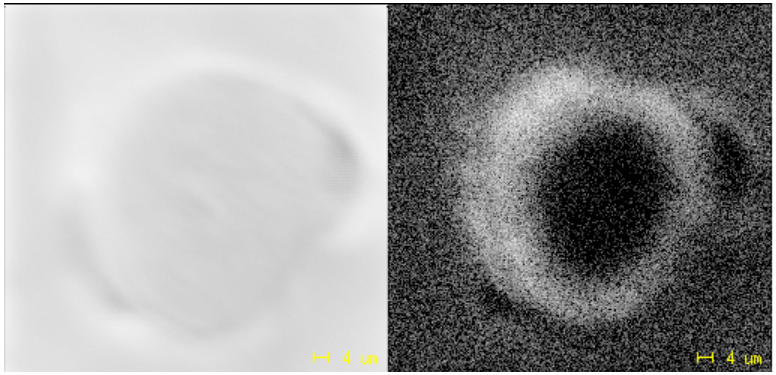


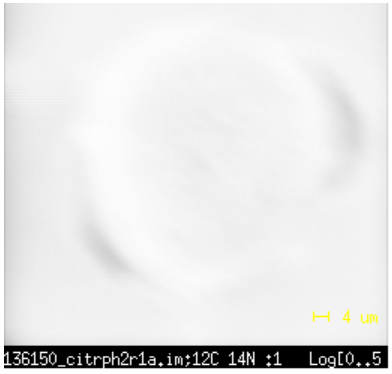
Sample 1 pH2 left on

Rinsed

Hair section - imaging



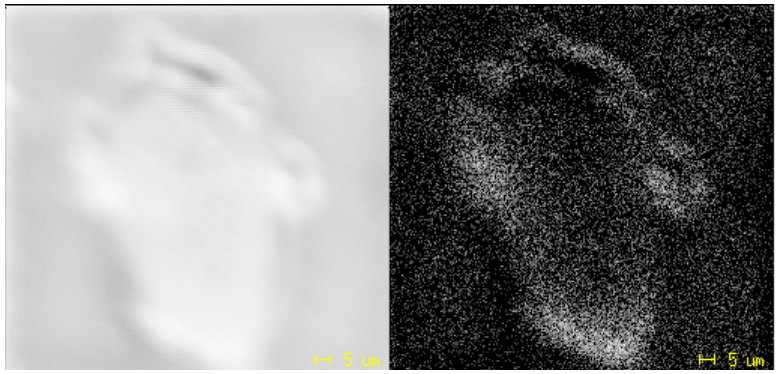


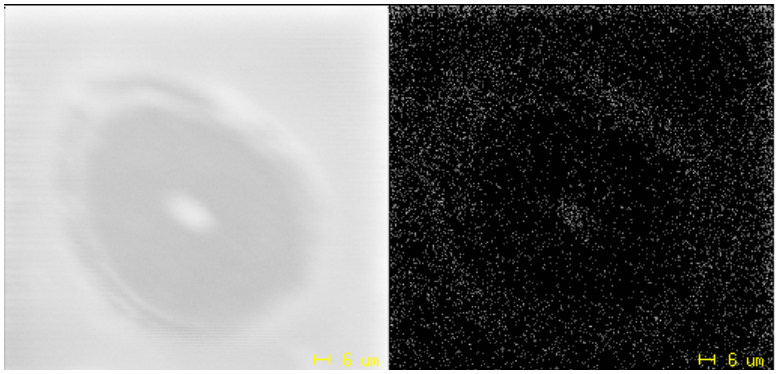


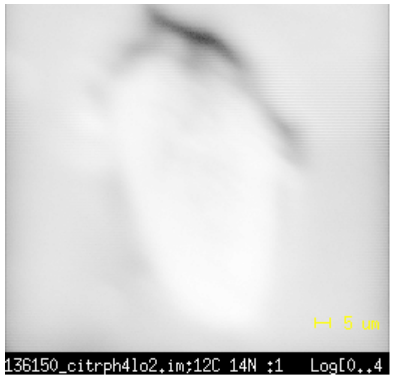
Sample 2 pH2 left on

Rinsed

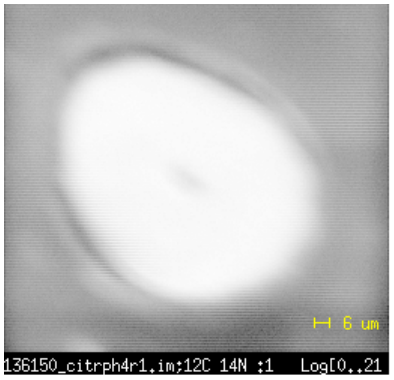
Hair section - imaging







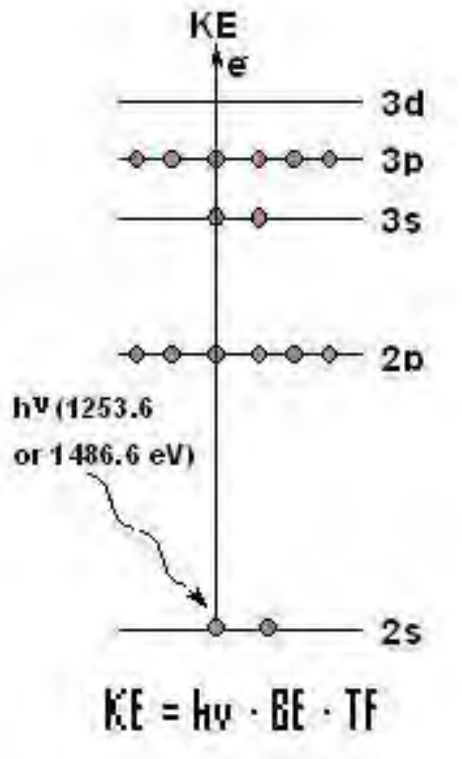
Sample 2 pH4 left on



Rinsed

X-Ray Photoelectron Spectroscopy (XPS)

- Soft x-ray irradiation
- Ejects core level photoelectrons
  Characteristic binding energy for elements
- Outer level electron relaxes to fill hole
- X-rays emitted
- Internally captured Auger
  electron emitted

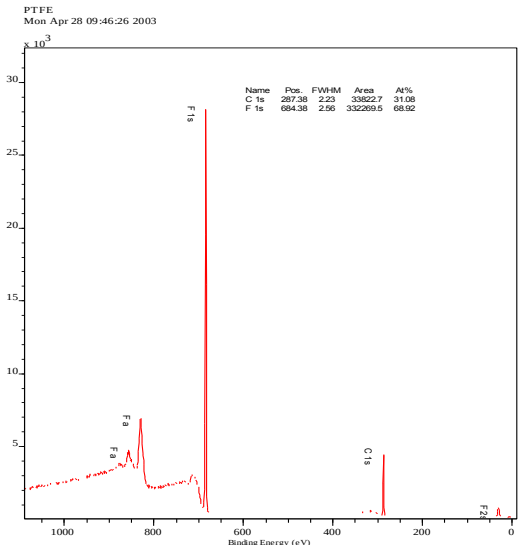


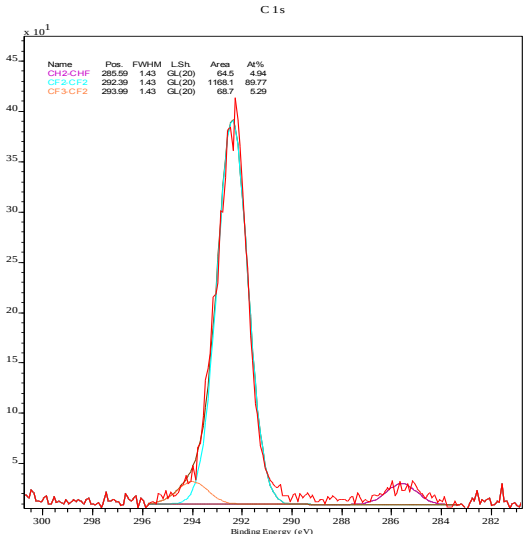
X-Ray Photoelectron Spectroscopy (XPS)

- Identification of all elements (except H and He)
- Conductors/insulators
- Elemental + chemical/oxidation states
- **Quantification**
- Surface specific (sampling depth <10nm)
- Surface imaging
- Depth profiling

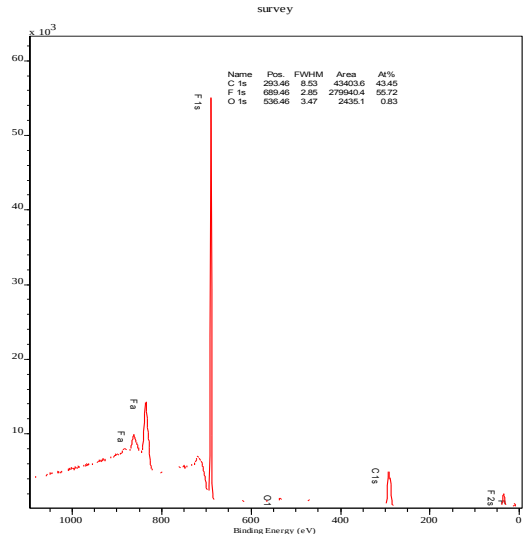
- Complementary technique to ToFSIMS which is more molecular specific

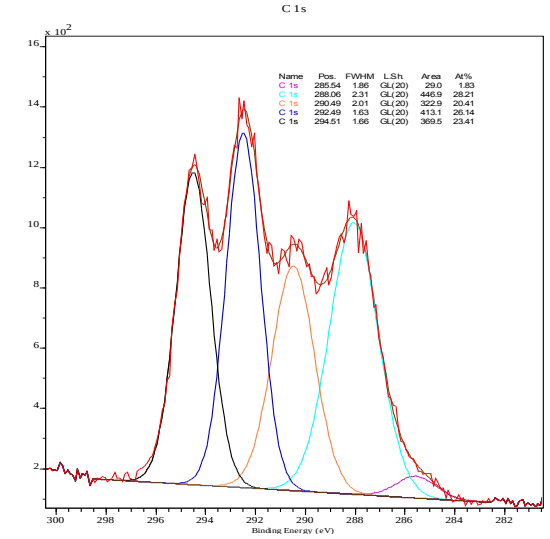
Spectroscopy





PTFE





Complex fluorocarbon

Survey spectra

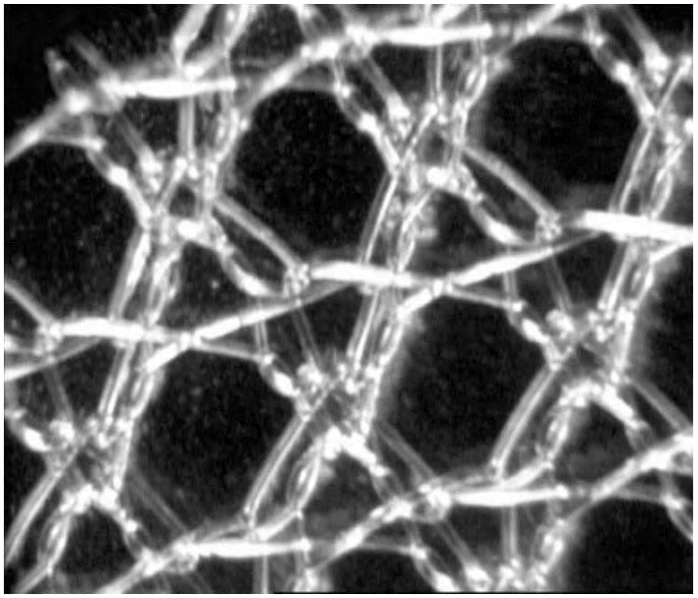
High resolution spectra

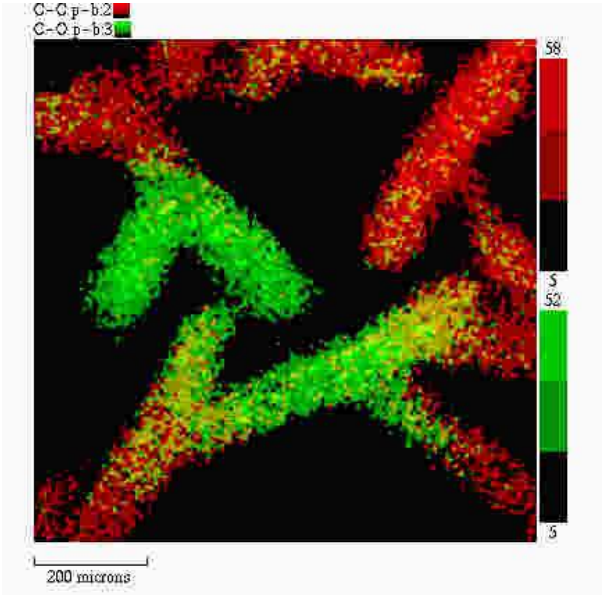
Quantification table output

	Tarnished Fluoropolymer coated samples					
Element	2-B1	2-B2	2-C1	2D-1	1-BC1	1-DE1
Carbon	32.9	32.4	35.0	34.8	33.6	35.5
σ	0.4	0.4	0.4	0.4	0.4	0.4
C-H/CH-CF	2.0	1.7	3.4	4.1	2.5	3.9
C-O/CH-CF_2	1.5	1.2	1.8	1.6	1.6	1.7
C=O/CF	2.6	2.4	2.8	2.9	2.9	2.9
CF_2	23.4	23.8	24.2	23.7	24.1	24.1
CF_3	3.3	3.3	2.8	2.5	2.6	2.9
Fluorine	65.3	66.4	62.2	62.2	64.2	61.6
σ	0.4	0.4	0.4	0.4	0.4	0.4
Oxygen	1.9	1.2	2.9	3.1	2.2	2.9
σ	0.2	0.2	0.2	0.2	0.2	0.2
C-O-C	1.3	0.8	2.3	2.5	1.6	2.4
O-CF_2	0.6	0.4	0.5	0.6	0.7	0.5
C-C/(CF_2 + CF_3)	0.075	0.063	0.125	0.154	0.092	0.142
Tarnish Index	2	4	5	5	6	5
Lucideon File	***E5F0601***	***E5F0602***	***E5F0603***	***E5F0604***	***E5F0607***	***E5F0608***

XPS imaging

Polypropylene mesh





Max. spatial resolution 3µm

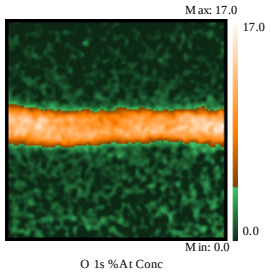
PP substrate = red

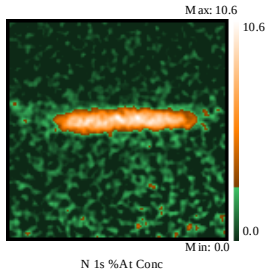
PEO coating = green

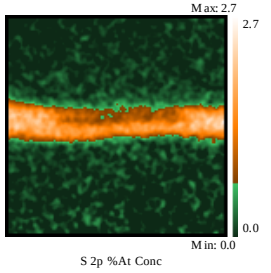
Hair section

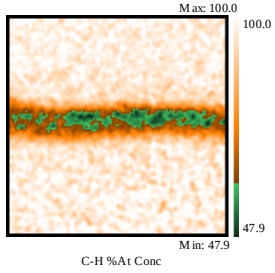
~800µm x 800µm

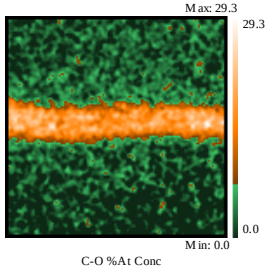
- Hair embedded in epoxy resin between PE plates
- Magnification of the section due to angle cutting

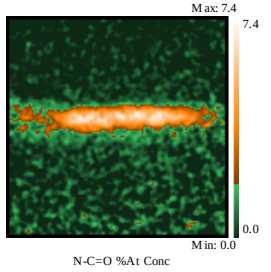










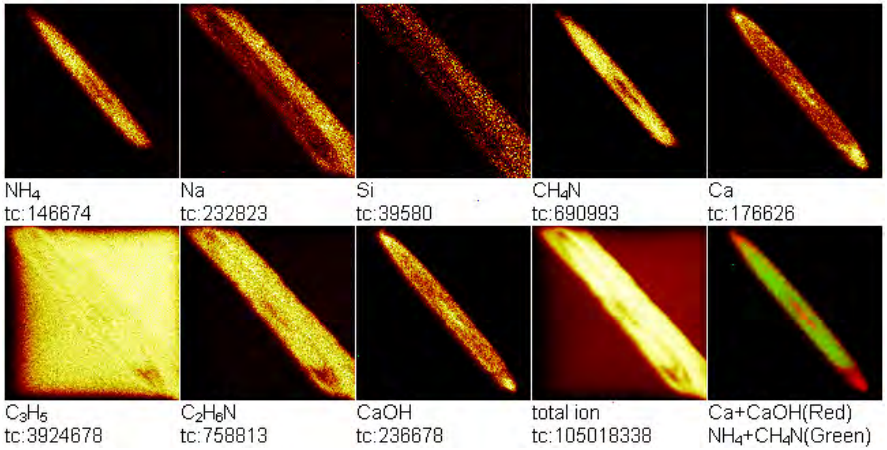


Spatial resolution 3µm, at best

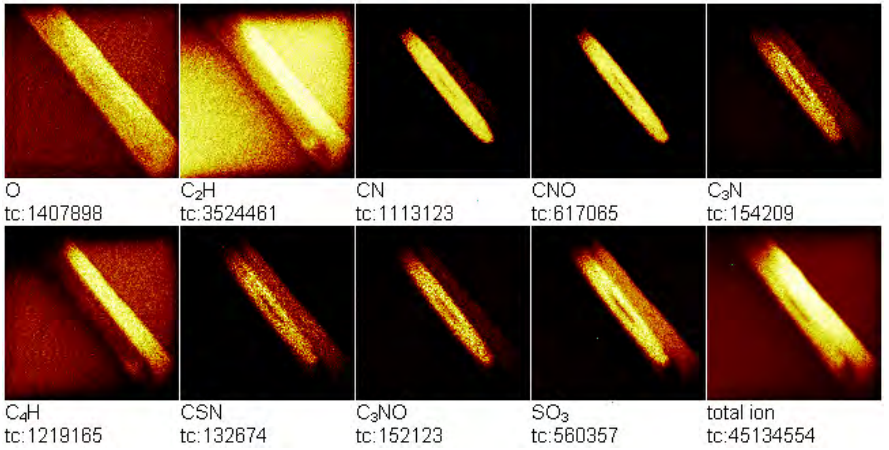
Hair section - XPS / ToFSIMS comparison

Low resolution

Field of view: 500.0 x 500.0 µm²; Hair cross-section

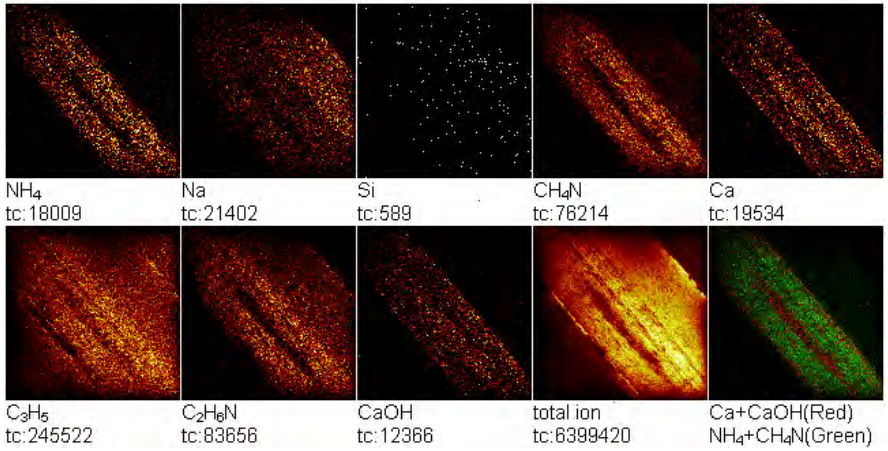


Field of view: 500.0 x 500.0 µm²; Hair cross-section

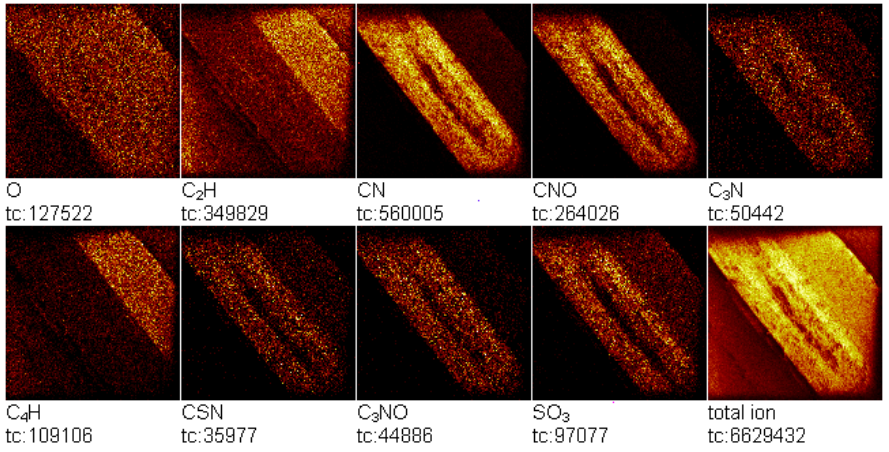


High resolution

Field of view: 150.0 x 150.0 µm²; Hair cross-section



Field of view: 150.0 x 150.0 µm²; Hair cross-section



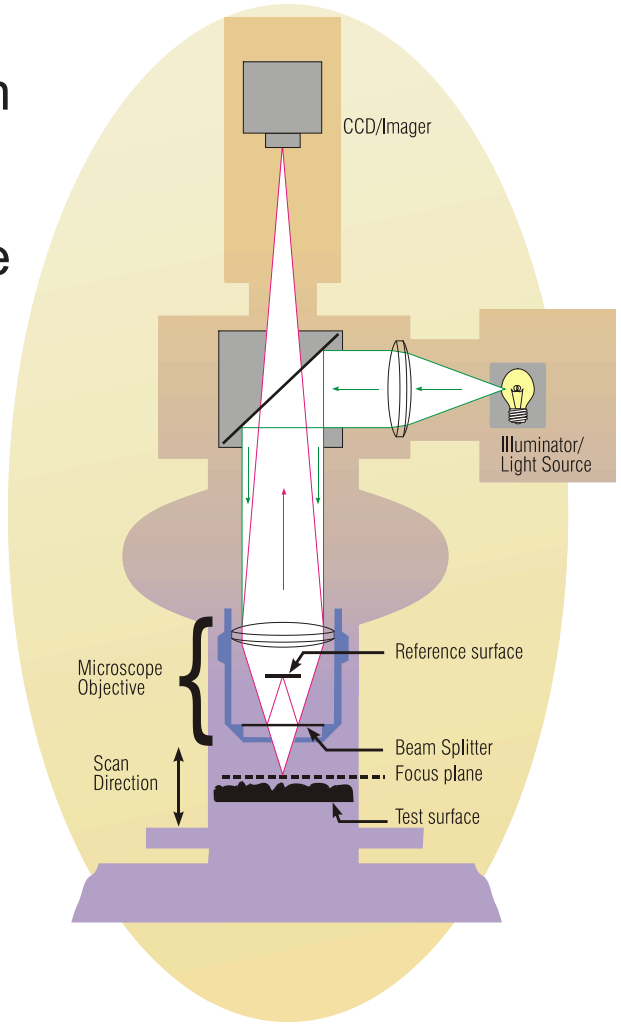
Metrology

- Optical microscopy / SEM have limited topographical information - qualitative
- Need to quantify the topography
- Historically, contact method such as stylus profilometry used but can be problematic for soft materials with damage to the surface investigated
  - Also, only 2D line scans were measured
- Investment in non-contact profiling techniques

3D non-contact profiling by WLI

- Conventional bright-field microscope with an interferometer objective
- A *non-contact* 3D surface profiling technique utilising white light interferometry (WLI)
- High spatial and depth resolution in combination with a wide scanning area

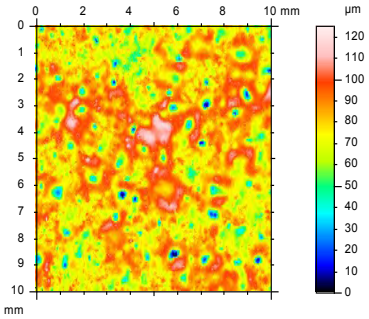
Height resolution ~1nm
Lateral resolution 0.5µm
Samples ~100µm to >10cm
Field of view 60µm to >10cm



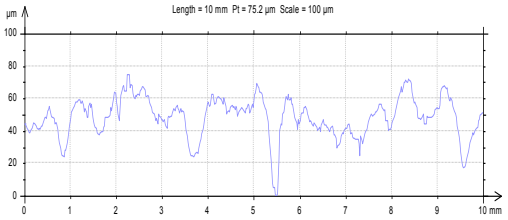
3D non-contact profiling by WLI

Quantitative measurement of surface topography and film thickness

Pseudo-colour height map

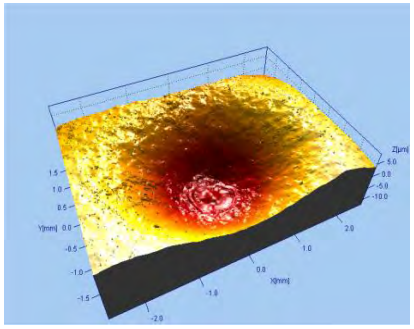


Line profiles

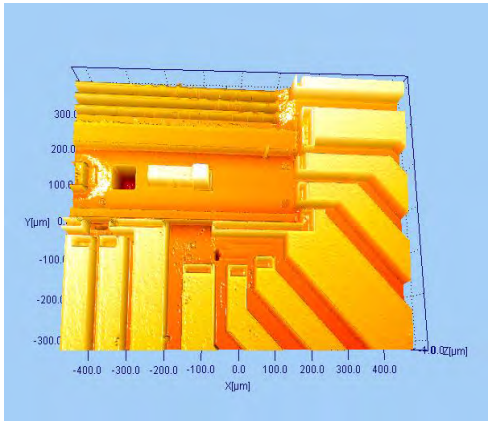


Amplitude Parameters	
Sa	10.6µm
Sq	14.0µm
Sp	43.4µm
Sv	79.5µm
St	123µm
Ssk	-0.752
Sku	4.82
Sz	118µm

3D view

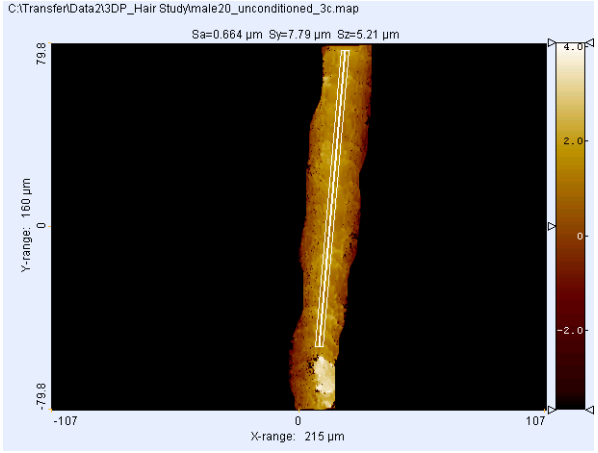


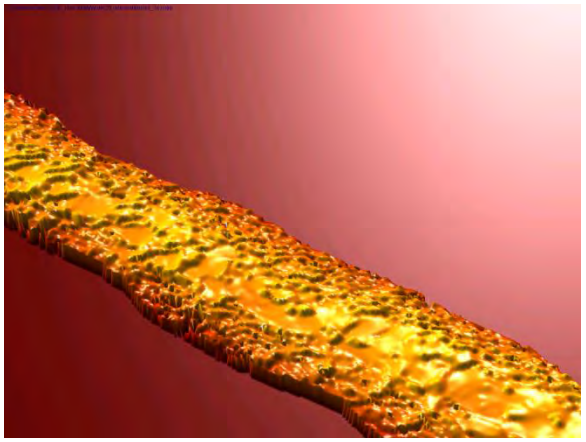
3D movie

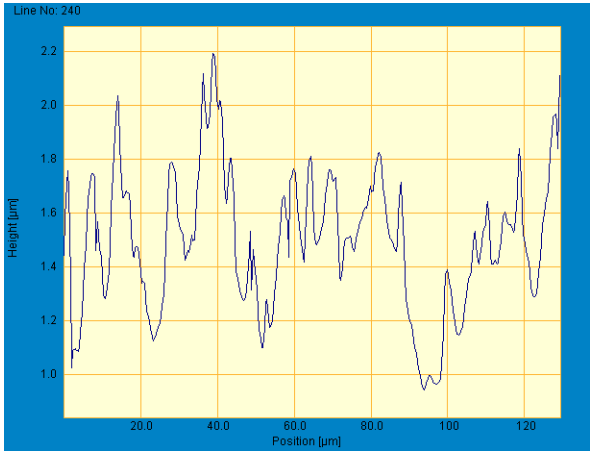


Roughness parameters, grain and pore analysis, transparent film thickness; sample replication

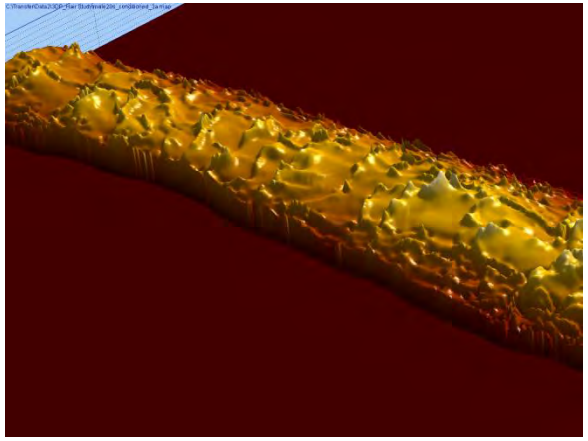
Effect of conditioning

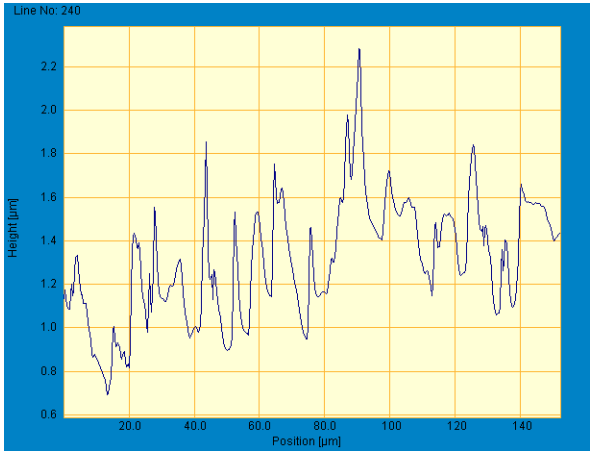






Unwashed hair 48 hours





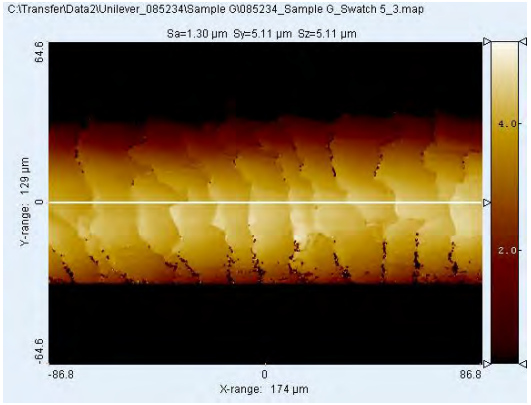
Conditioned hair

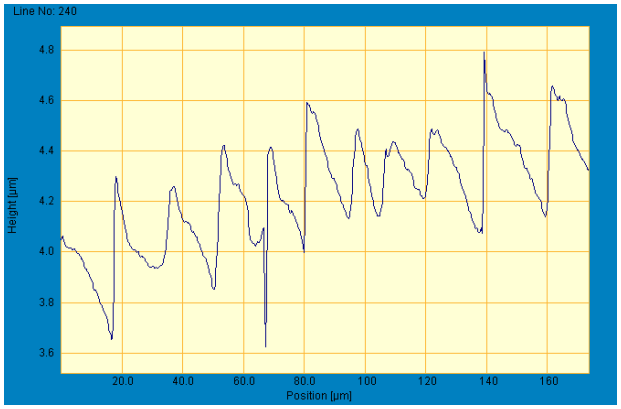
Effect of conditioning: roughness parameters

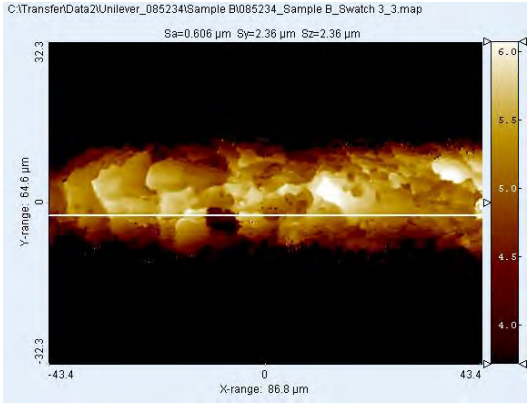
Description	Sample	Reading	Ra	Ry	Rz	Sample Mean Ra	Sample Mean Ry	Sample Mean Rz	Batch Mean Ra	Batch Mean Ry	Batch Mean Rz
Male 50s		a	0.27	1.64	1.30	0.25	1.45	1.20	0.25	1.45	1.20
		b	0.23	1.24	1.10						
	1	c	0.25	1.46	1.20						
Female 20s Conditioned		a	0.24	1.76	1.53	0.21	1.34	1.13	0.21	1.34	1.13
		b	0.19	0.98	0.86						
	1	c	0.20	1.27	1.01						
Female 20s Blonde Dyed		a	0.16	1.10	0.91	0.20	1.22	0.99	0.20	1.22	0.99
		b	0.29	1.65	1.30						
	1	c	0.15	0.90	0.75						
Male 20s Conditioned		a	0.189	1.38	1.06	0.18	1.25	1.02	0.19	1.28	1.01
		b	0.143	0.861	0.75						
	1	c	0.209	1.5	1.25						
		a	0.186	1.3	0.911	0.19	1.25	0.95			
		b	0.221	1.27	1.01						
	2	c	0.168	1.18	0.931						
		a	0.225	1.59	1.13	0.22	1.69	1.25			
		b	0.214	1.72	1.27						
	3	c	0.235	1.76	1.35						
		a	0.209	1.35	1.14	0.19	1.11	0.94			
		b	0.177	0.909	0.814						
	4	c	0.177	1.06	0.875						
		a	0.186	1.32	0.982	0.17	1.13	0.86			
		b	0.139	0.98	0.726						
	5	c	0.17	1.09	0.885						
Male 20s Unwashed (48 hours)		a	0.196	1.6	1.08	0.25	1.63	1.29	0.22	1.41	1.11
		b	0.345	1.8	1.53						
	1	c	0.223	1.5	1.25						
		a	0.219	1.57	1.22	0.22	1.58	1.15			
		b	0.235	1.93	1.31						
	2	c	0.207	1.25	0.916						
		a	0.26	1.51	1.26	0.22	1.31	1.07			
		b	0.189	1.18	0.909						
	3	c	0.205	1.25	1.04						
		a	0.188	1.36	0.883	0.19	1.28	0.96			
		b	0.215	1.45	1.1						
	4	c	0.168	1.02	0.885						
		a	0.225	1.13	1.04	0.23	1.23	1.07			
		b	0.266	1.62	1.31						
	5	c	0.185	0.94	0.871						

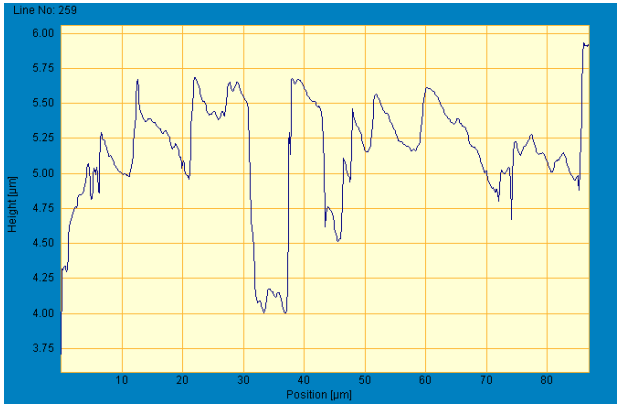
Decrease in roughness values by 9% – 13% upon conditioning

Scale height and particle measurement

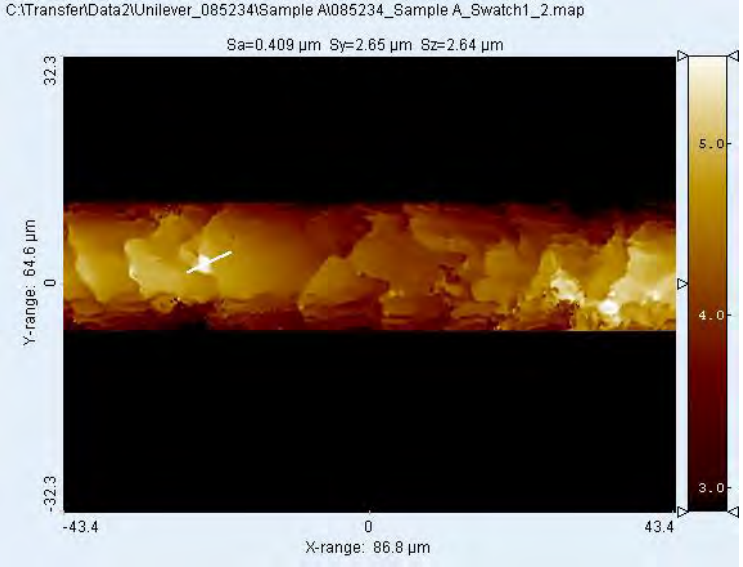




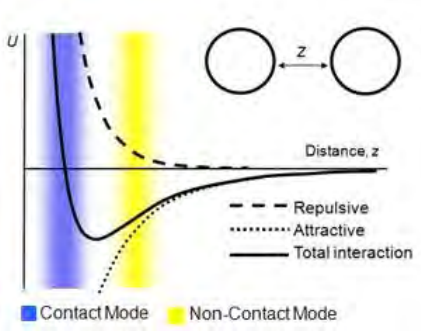


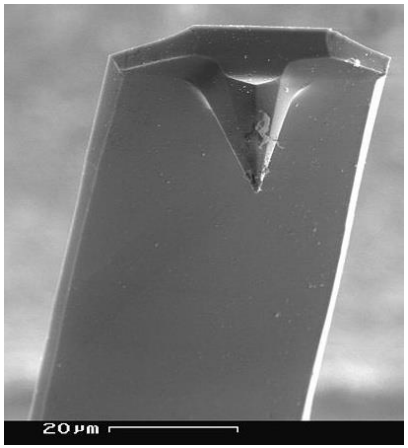


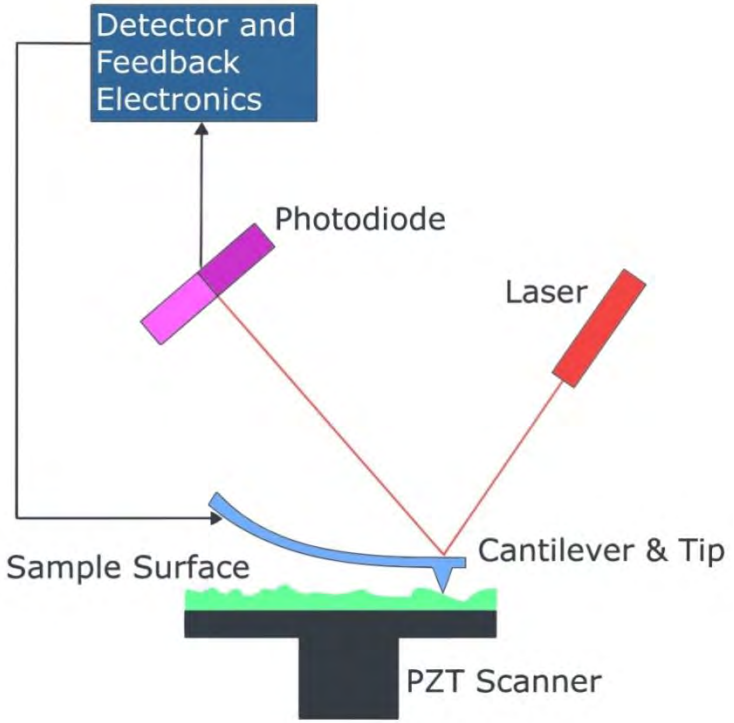
Scale height and particle measurement



Atomic force microscopy







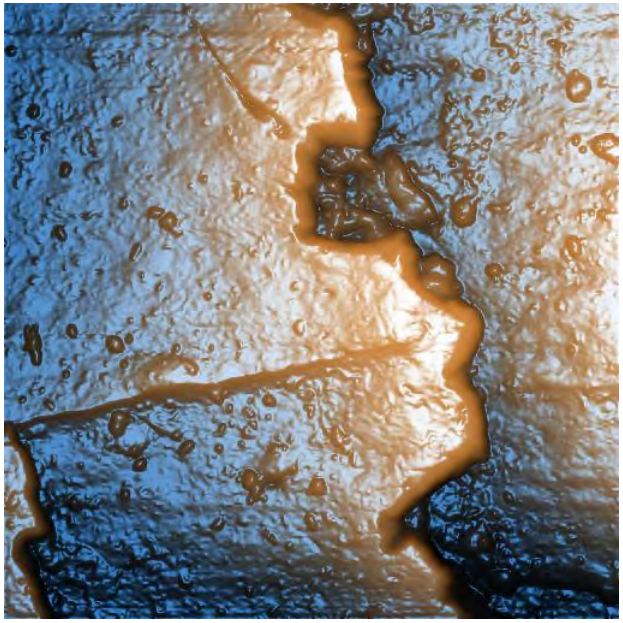
Common AFM modes

- Surface topography
  - (Contact and non-contact modes)
- Friction force
  - (Lateral force measurement)
- Hardness
  - (Force v distance curves)
- Electrical conductivity
- Magnetic force

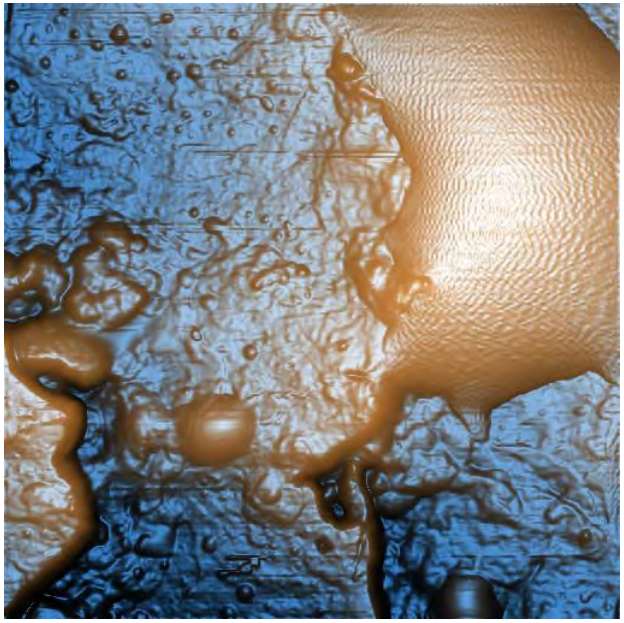
- SEM resolution but in air or under liquids

AFM of human hair (10 microns scan)

Before conditioner

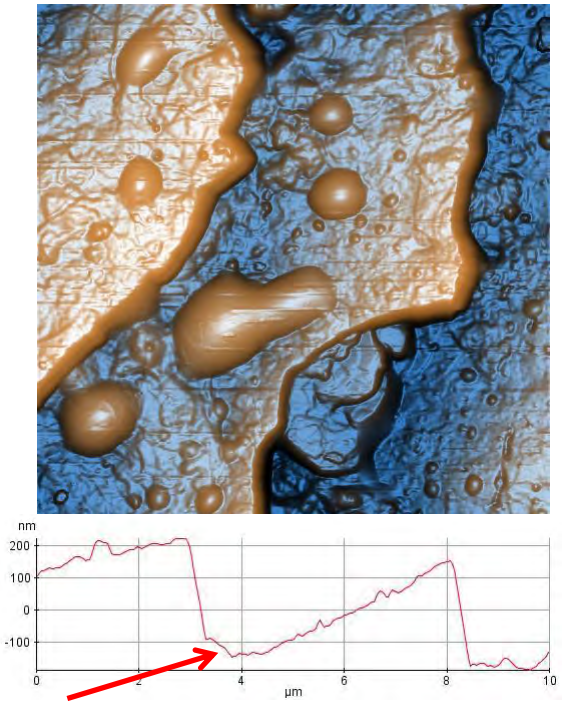


After conditioner



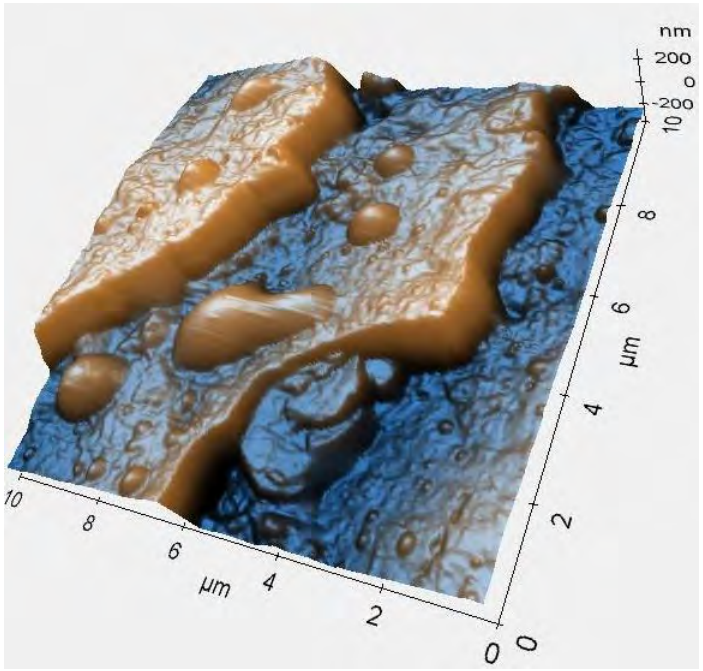
AFM of human hair (10 microns scan)

After conditioner

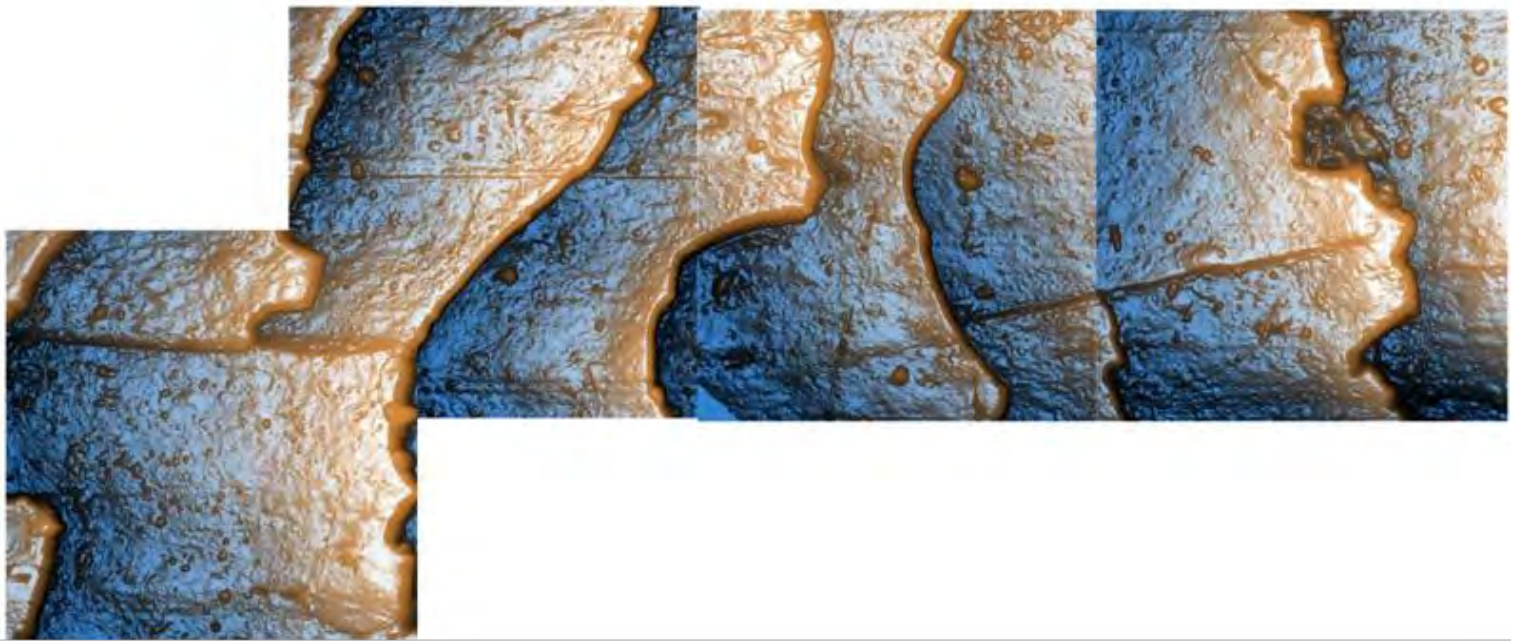


Line trace

Isometric view



Stitched images



Any questions?

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Thank you

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