Improving the accuracy of optical surface topography measuring instruments

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INTDS/TFW, Mainz, Germany
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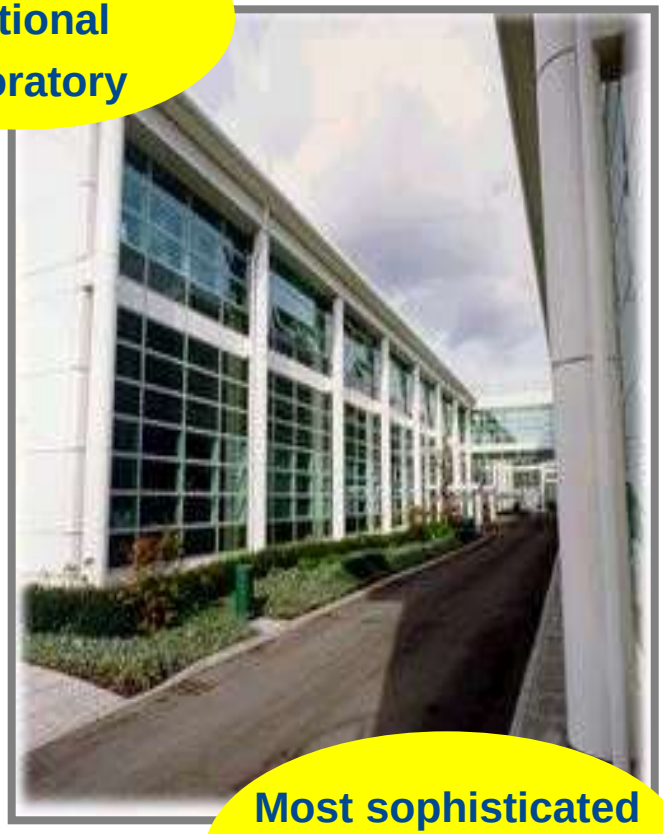
About NPL …

NPL
National Physical Laboratory

- The UK's national standards laboratory
- Founded in **1900**
- World leading **National Measurement Institute (NMI)**
- 600+ specialists in **Measurement Science**
- State-of-the-art standards facilities
- The heart of the UK's **National Measurement System** to support business and society
- Experts in **Knowledge Transfer**
- A very successful **GOCO**
- Managed by **Serco** since **1995**

36,000 m² national laboratory

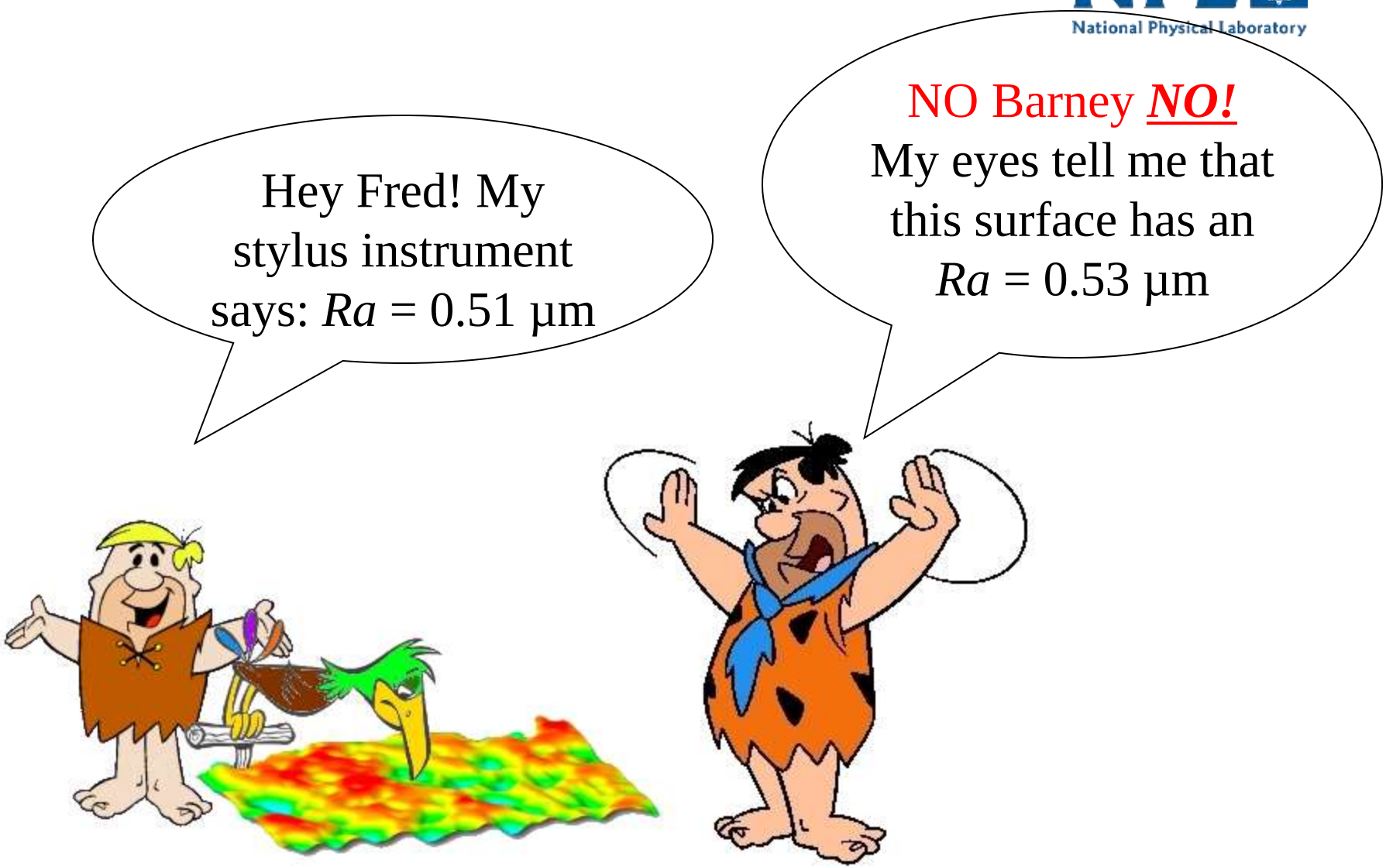


Most sophisticated measurement science building in the world

Talk structure

- Context
- An important concept
- Traceability for areal surface topography
- Optical measurement of surface topography
- Linear systems theory approach to calibration
- Removal of systematic errors
- Future work

Context


Hey Fred! My stylus instrument says: *Ra* = 0.51 µm
NO Barney ***NO!***
My eyes tell me that this surface has an *Ra* = 0.53 µm

An important concept – traceability

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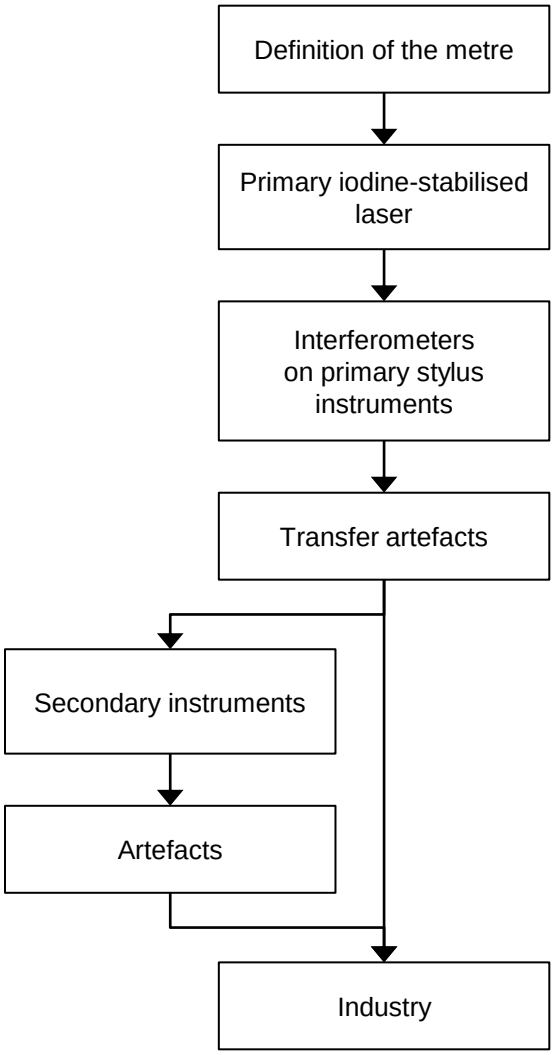
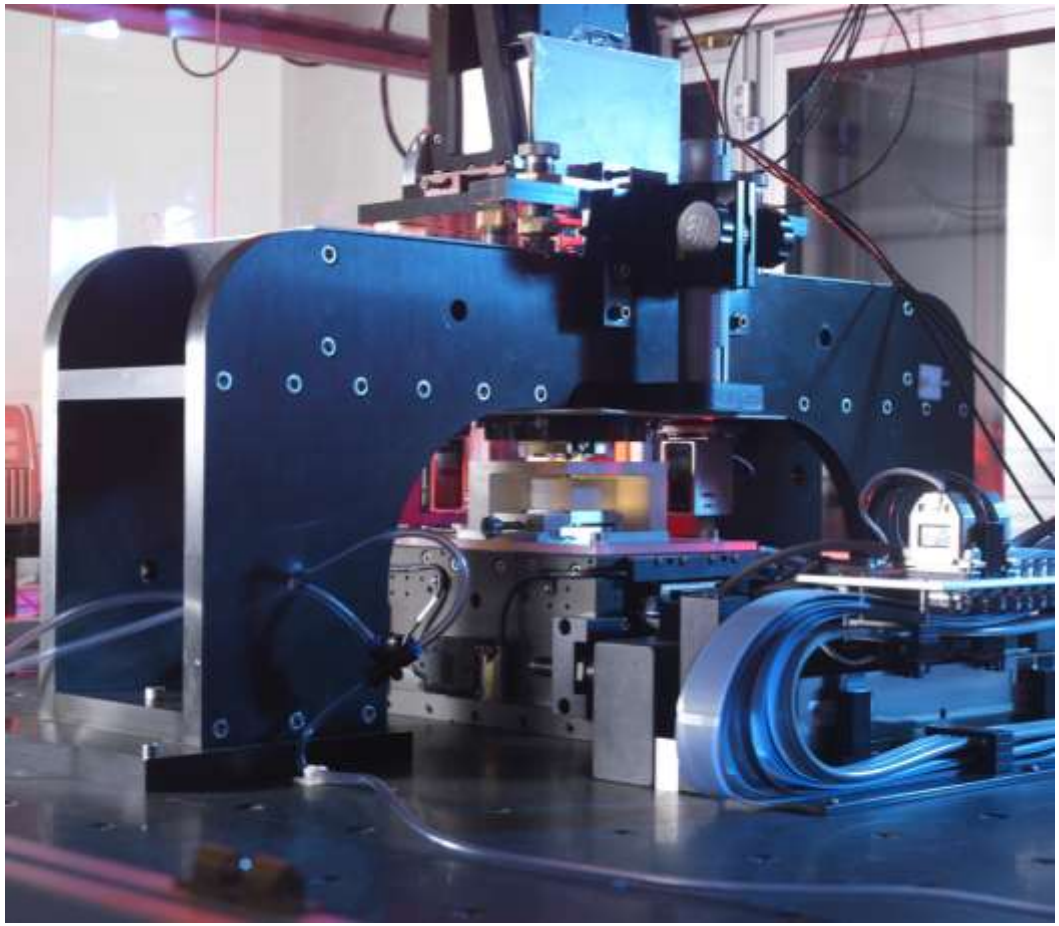
"property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons **all having stated uncertainties**"

Iodine-Stabilised He-Ne laser

Traceability – surface metrology





Leach R K *et al* (2009) *Meas. Sci. Technol*. **20** 125102

Areal surface topography measuring instruments

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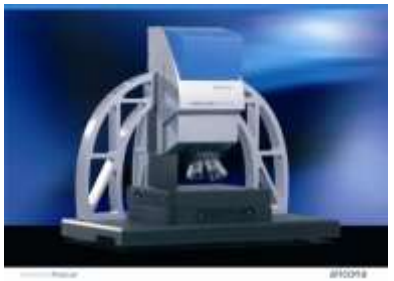
Tactile and non-contact instruments

- Tactile – contact stylus instruments
- Non-contact – optical instruments



Where are ISO areal surface topography standards?

National Physical Laboratory

- ISO 25178 parts 2 (parameters), 3 (specification operators), 6 (instruments), 601/701 (stylus instruments), 602 (chromatic confocal) are published

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- Then there are parts 602, 603, 604, 605, 606, 607, … in progress and unless we stop this proliferation, there will be many more!
- NPL and Zygo is drafting *one* part 600 that will cover the metrological characteristics and calibration of *all* instruments
- I then propose we make the 60X standards technical specifications

How do we calibrate areal instruments?

- Draft ISO standards will cover the calibration of certain *metrological characteristics.* These are currently:

  Noise

  Residual Flatness

  Straightness, squareness and linearity of scales

  Resolution (lateral period limit)

- These will (hopefully) be common across all areal instruments
- Also need software measurement standards

Giusca *et al.* 2012 Calibration of areal surface topography measuring instruments. Parts 1 and 2 (2012) *Meas. Sci. Technol.* **23** 035008 and 065005

Resolution in ISO 25178

- Lateral resolution simply given by the Rayleigh or Sparrow limits (or Abbe depending on coherence)

Resolution in ISO 25178

National Physical Laboratory

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- The term “lateral period limit” is proposed for the 3D resolution or the ability to resolve two objects on a surface plus measure the correct height
- Lateral period limit is defined as the 50 % cut-off point from the instrument transfer function (see de Groot et al. *Opt. Photon. News*, April 2012)

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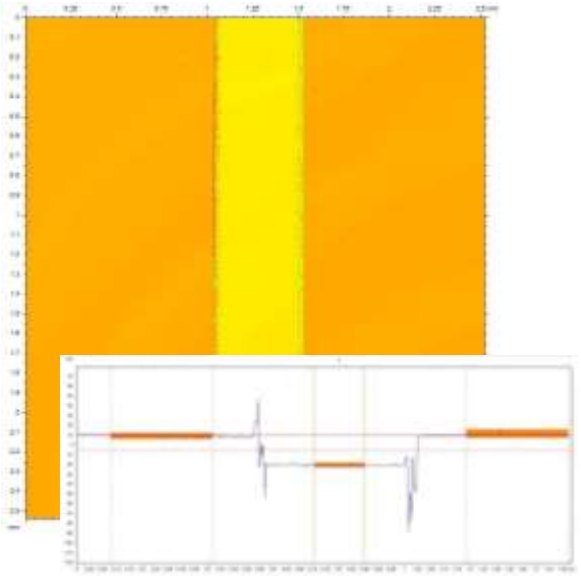
- But, much better off using the *optical* transfer function as this does not have the height restriction
- Also, watch out for new definitions of optical resolution!

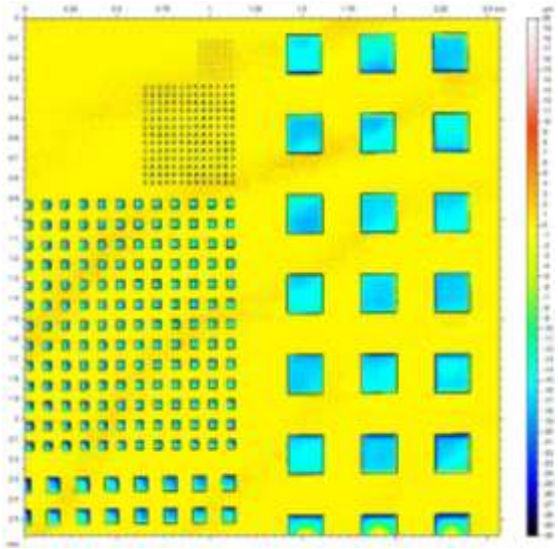
The “Areal Bento Box”

- NPL (with Rubert) producing a box of artefacts to allow calibration according to ISO 25178-600
- Artefacts manufacture using e-beam (KIT) and FIB (University of Surrey) writing, diamond turning (Bremen University) and electroform replication
- Manufacturing trials on plastic replication (with CRANN and University of Bradford)
- Contains: optical flat, step heights, lateral grids, star patterns, sphere on plane, deterministic
- Now publishing good practice guides for stylus, confocal, CSI and focus-variation

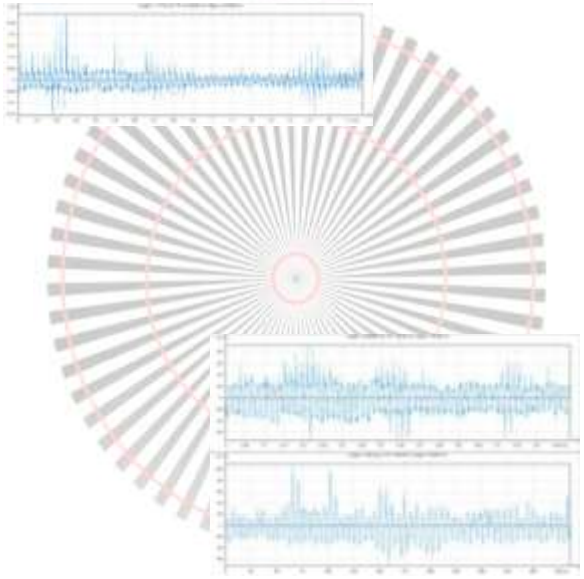
Step heights



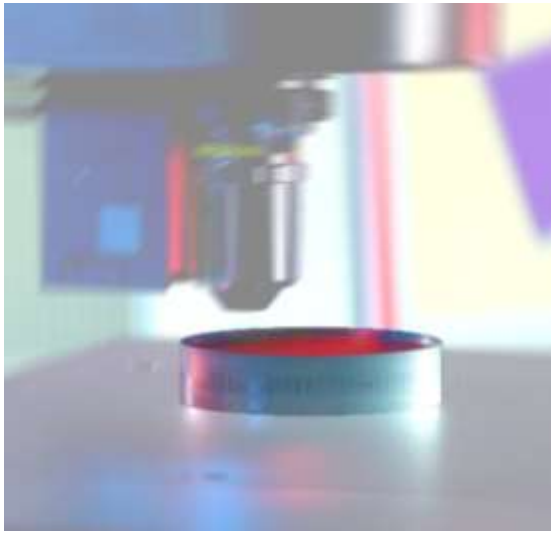
Cross gratings



Resolution artefact



Optical flat



Good Practice Guide

Recommended by NPL for your instrument

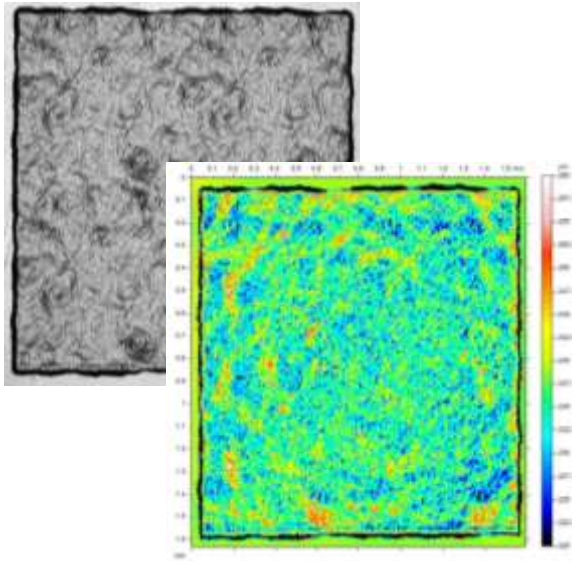
NPL Artefacts

for the calibration of the metrological characteristics areal surface texture measuring instruments to ISO 25178

National Measurement System

NPL National Physical Laboratory

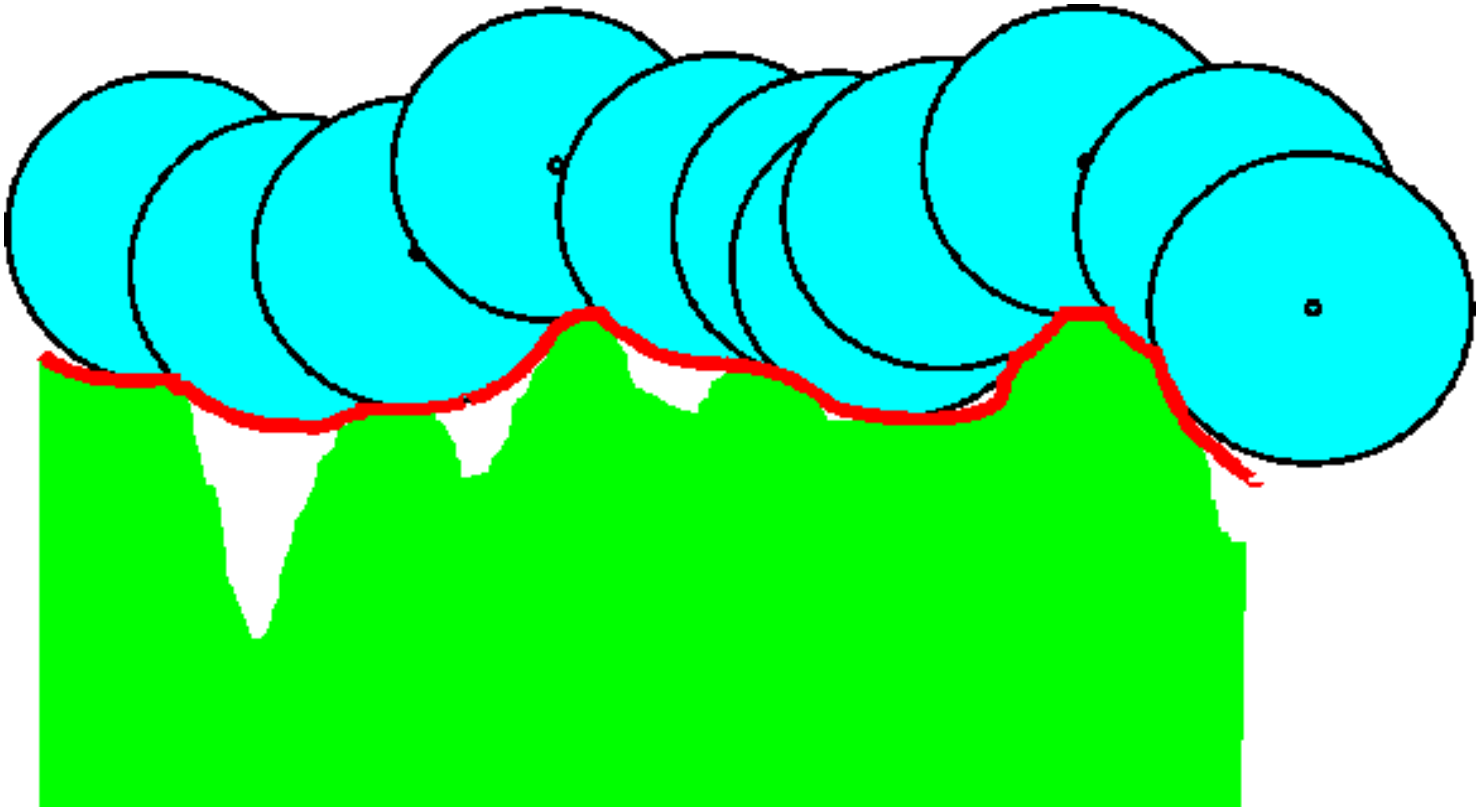
Deterministic artefact



So is that the job complete?

- Absolutely not!
- We can measure the scales (and construct uncertainty budgets) but does this mean we can measure a real surface?
- Surfaces are a complex combination of spatial frequencies (slopes) – we need to calibrate the spatial frequency response of the instruments
- But first some words about optical instruments

The mechanical surface



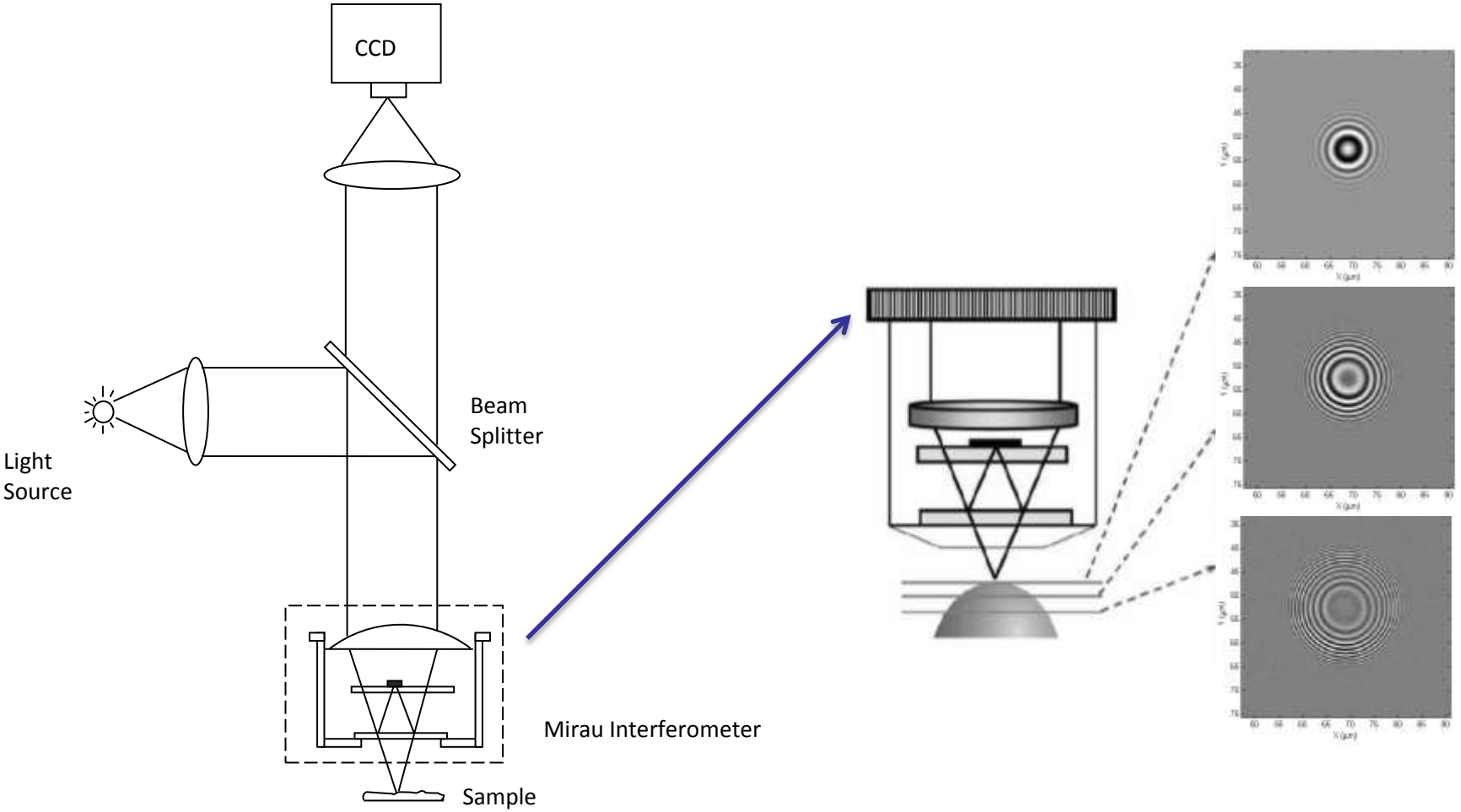
The optical surface

- ISO 25178-3 “the electromagnetic surface”
- What does this mean? Is it the same for an interferometer and a scattering instrument?
- Issues – wavelength dependence (dispersion), spot size, resolution/diffraction (of stars and of structures), material effects, multiple scattering….
- Often we assume linear conditions (Born approximation) when they do not always apply

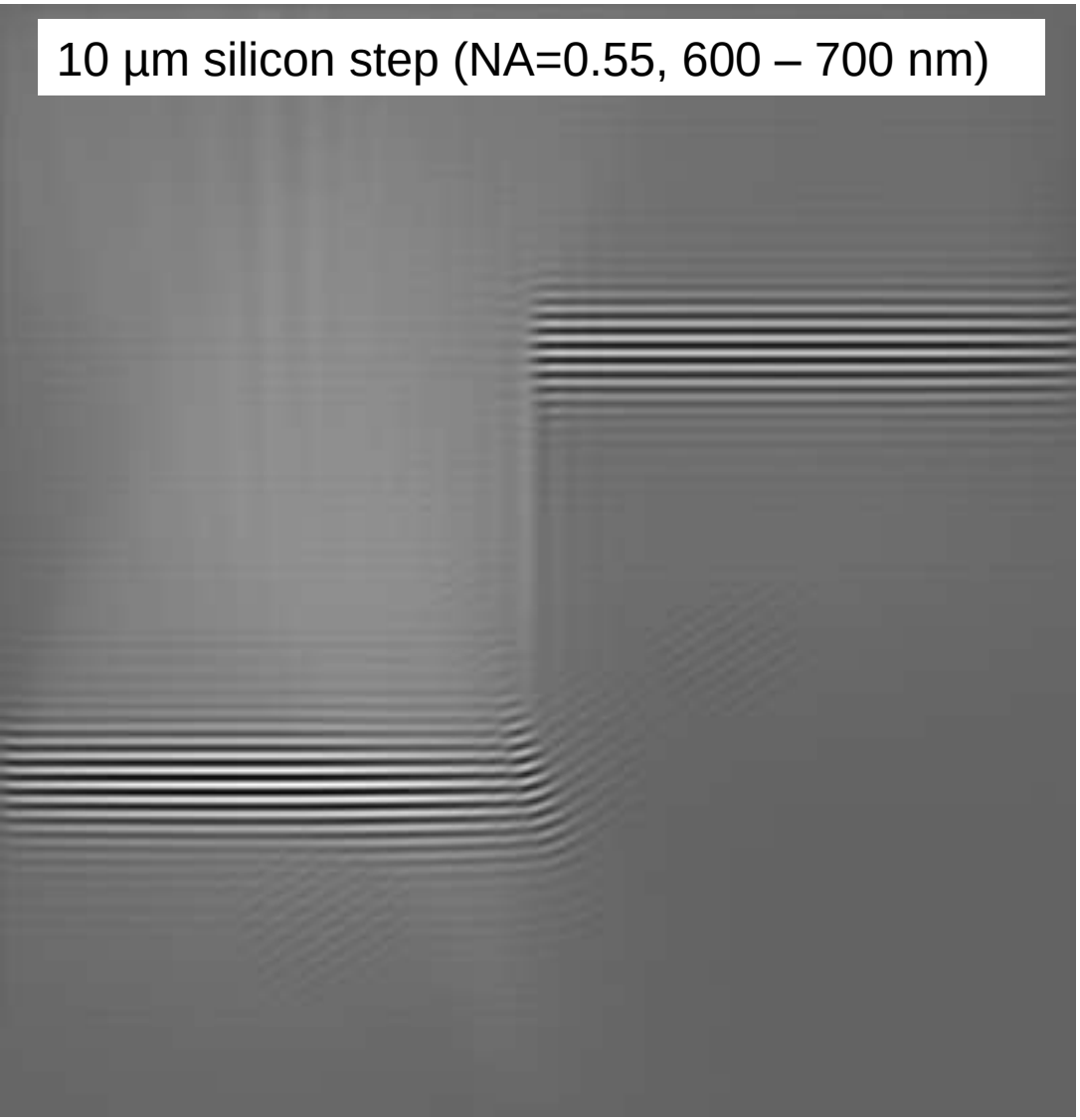
The optical surface

- “The boundary between two materials with different optical properties”
- Optical properties:
  - ε Permittivity
  - μ Permeability
  - σ Conductivity
- The change in optical properties governs the amplitude and phase of the light reflected and transmitted by the boundary according to Maxwell’s Equations

Optical example – coherence scanning interferometer (CSI)



Step Interferogram



The information present in the interferogram is related to the step height by estimating the position of peak visibility (called coherence scanning interferometry (CSI) mode), and/or the phase of the interference fringes (called phase shifting interferometry (PSI) mode).

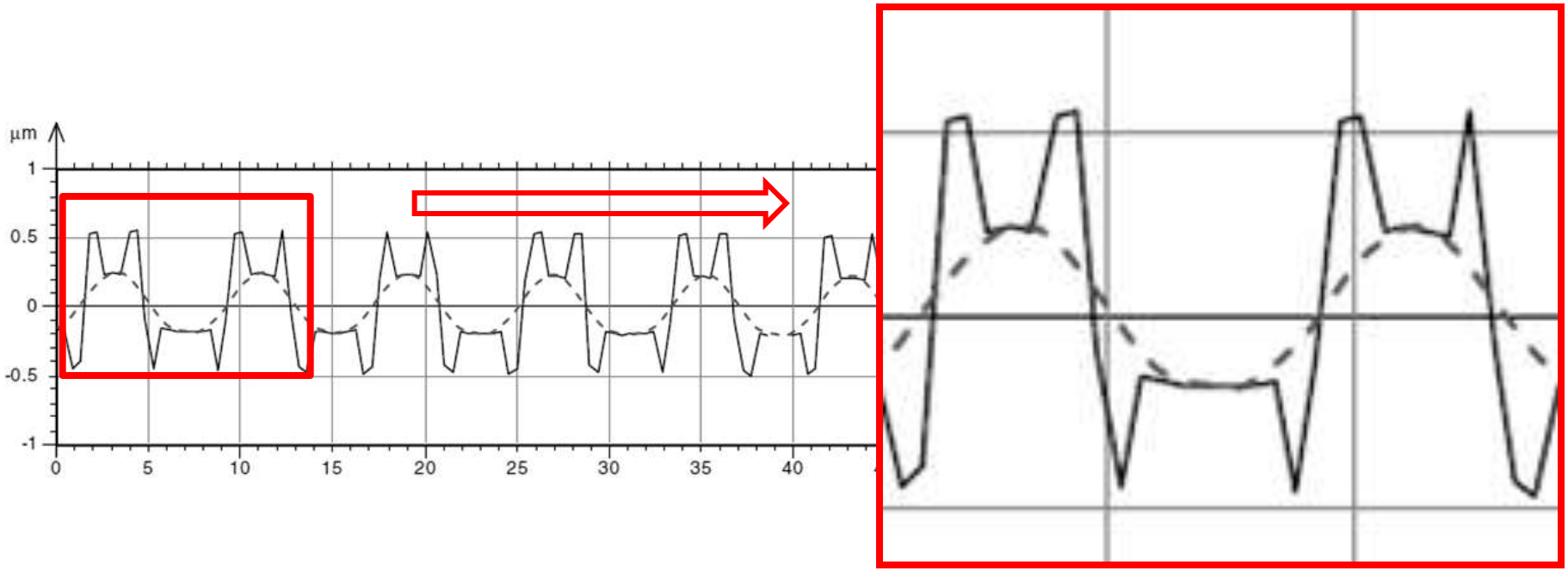
Some CSI limitations

- Edge artefacts – The Bat Wing Effect
- Ghost steps – dispersion effects
- Material effects
- Multiple scattering/surface roughness measurement

Gao F, Leach R K, Petzing J,Coupland M (2008) Surface measurement errors using commercial scanning white light interferometers *Meas. Sci. Technol*. **19**

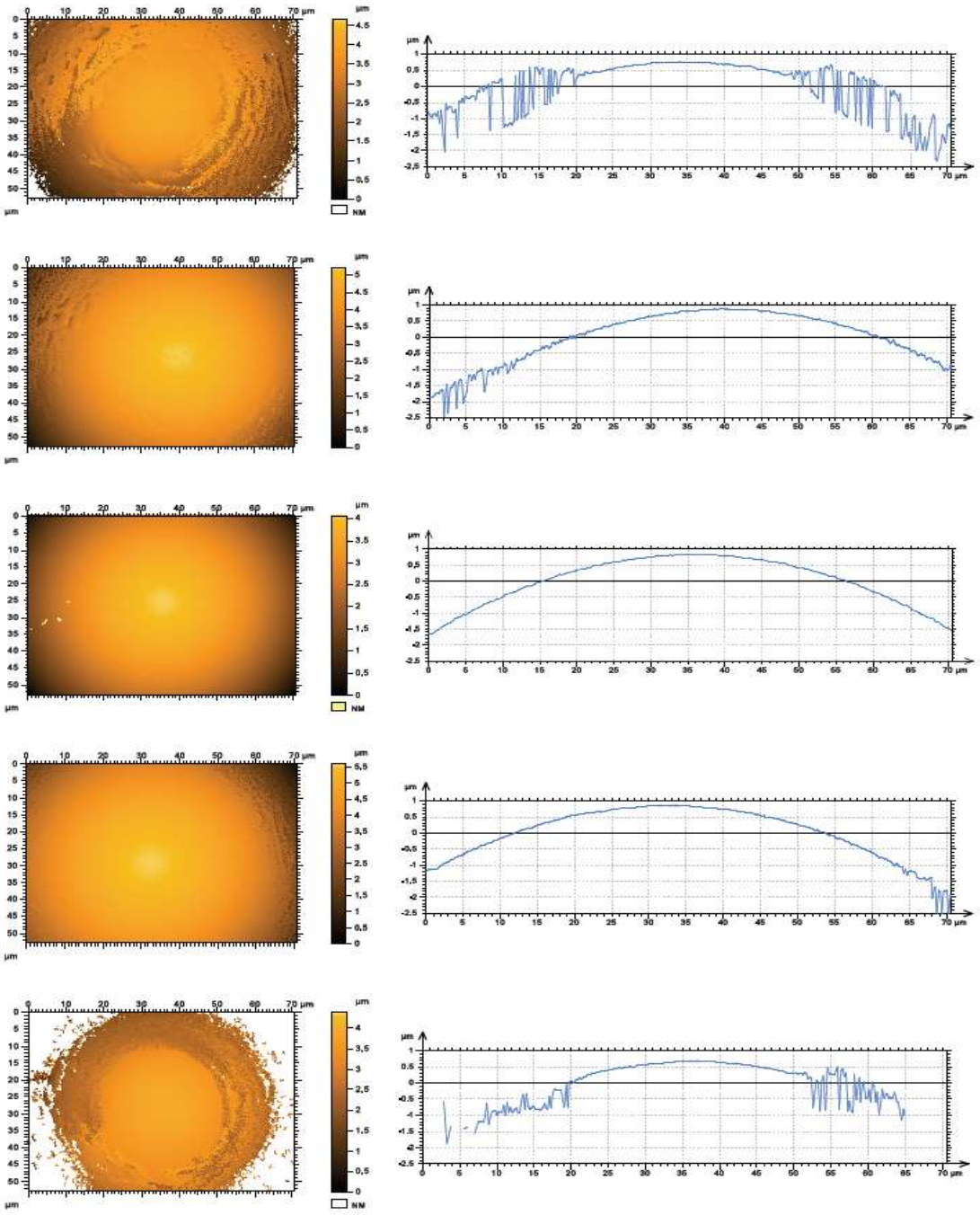
CSI measurement errors

- CSI shows problems measuring surface gradients.



- CSI measurement of sinusoidal grating of 8 µm pitch and 466 nm amplitude (peak to peak)

Focusing



Calibration – a two step process

1. Calibrate machine axes XYZ
   - Step heights
   - Lateral standards

Giusca C L, Leach R K, Helery F 2012 Calibration of the scales of areal surface topography measuring instruments: part 2. Amplification, linearity and squareness *Meas. Sci. Technol.* **23**

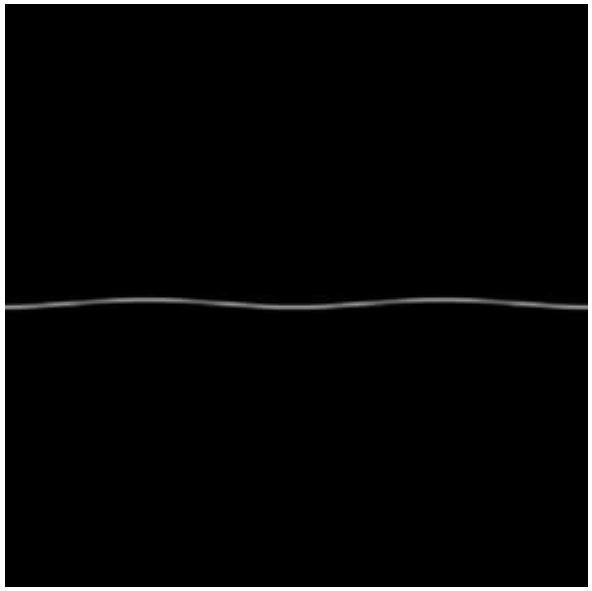
2. Point spread measurement

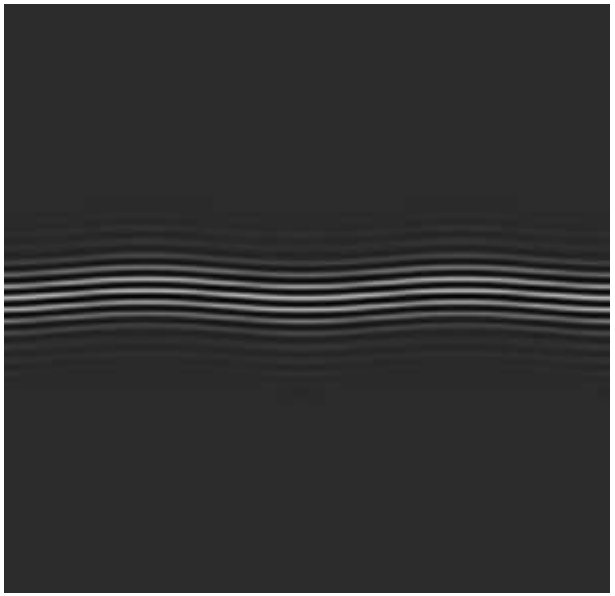
   Equivalent to “probe sphericity” - like a CMM

Adjustment

- Piezo look-up tables
- Distortion compensation
- Fringe pattern filtering

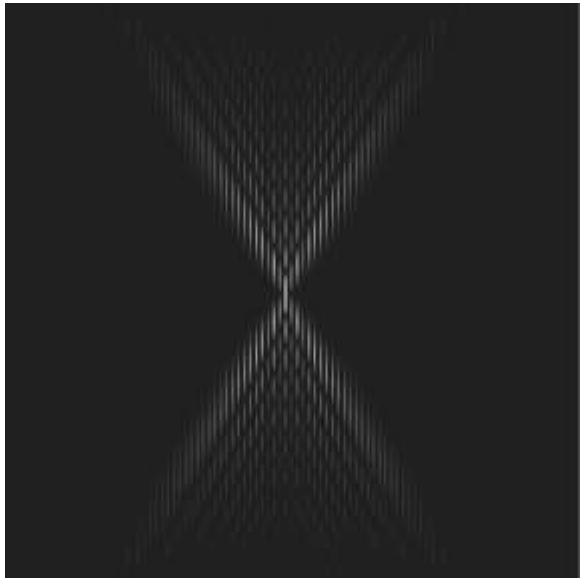
Foil model: space domain

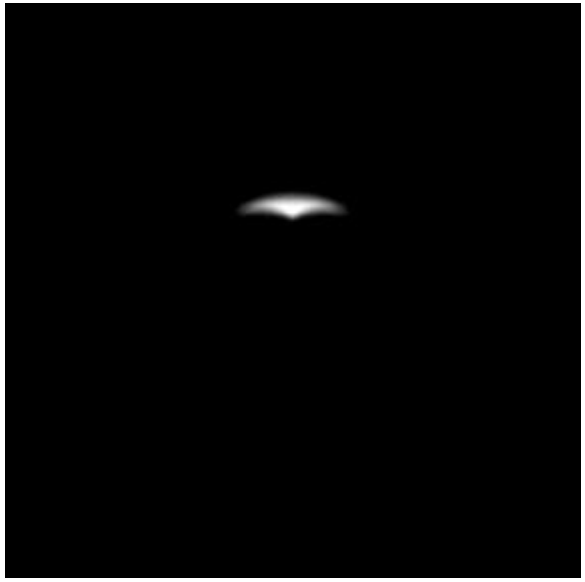


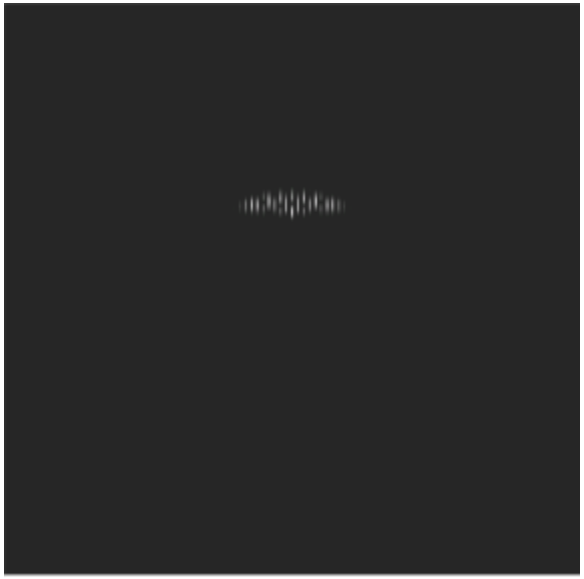


$$\text{Foil} \otimes \text{PSF} = \text{Fringes}$$

Foil model: frequency domain

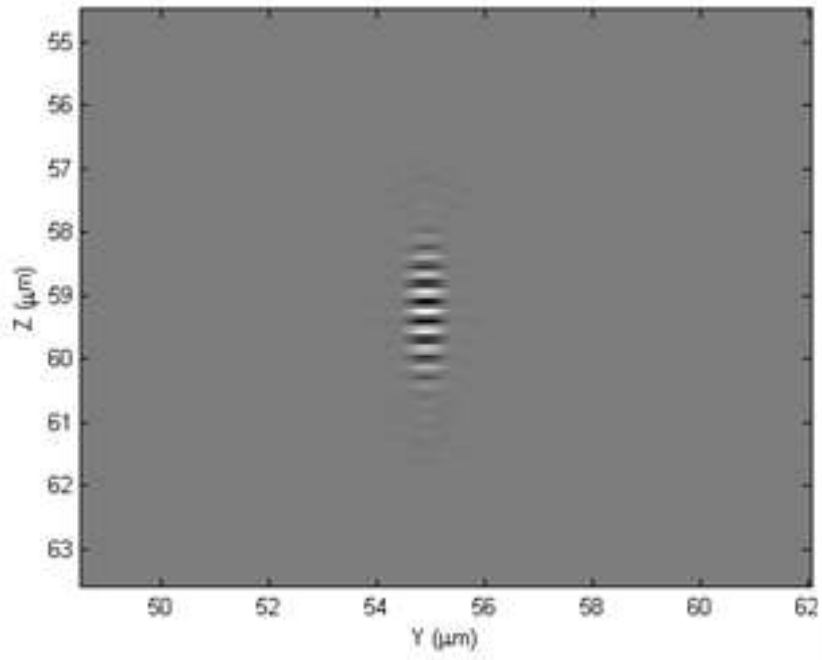




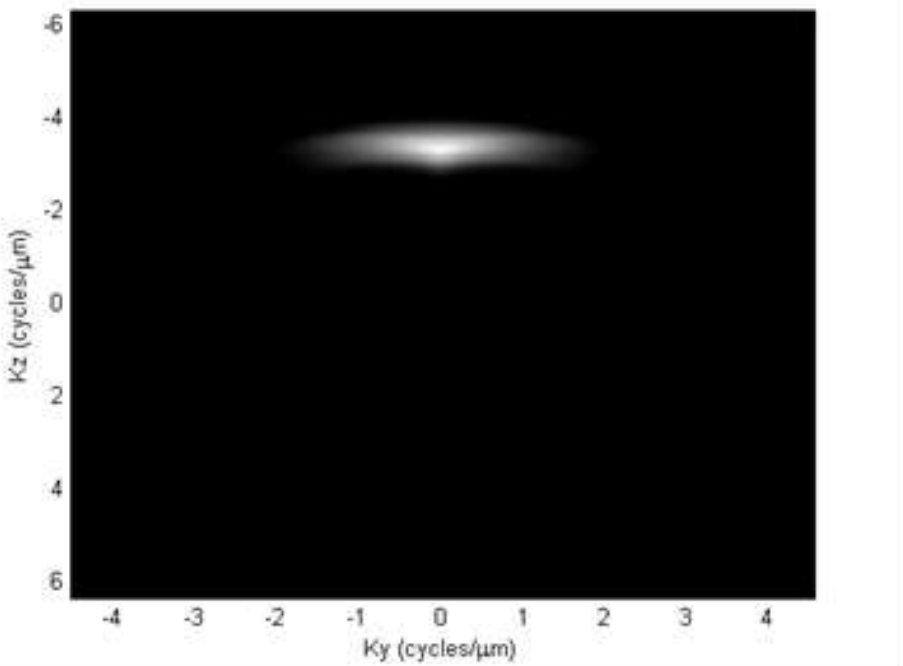


$$\mathrm{F.T.}\{\mathrm{Foil}\} \times \mathrm{TF} = \mathrm{F.T.}\{\mathrm{Fringes}\}$$

PSF and TF for an ideal CSI system

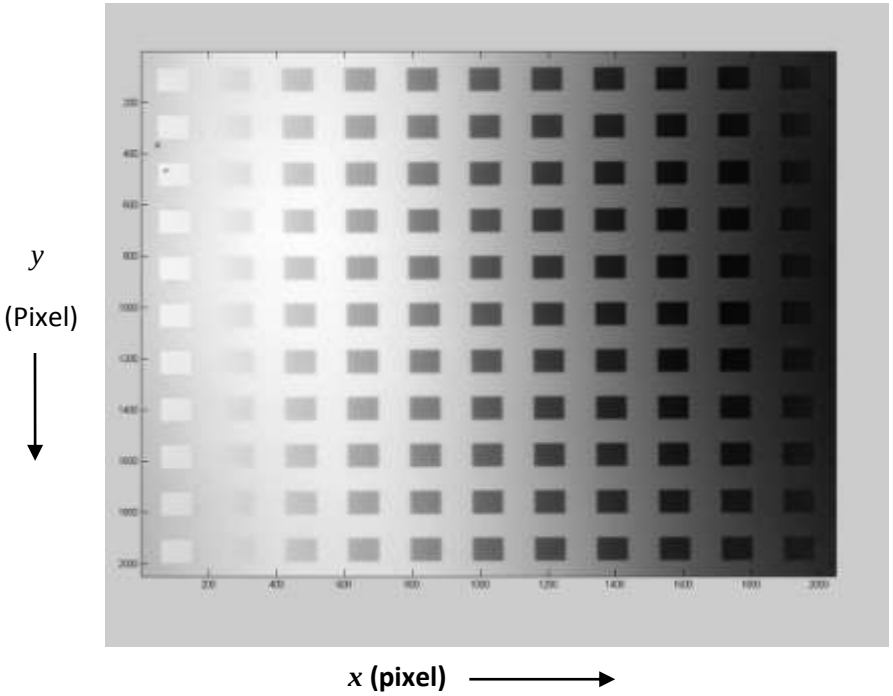


PSF (real part) for an ideal CSI

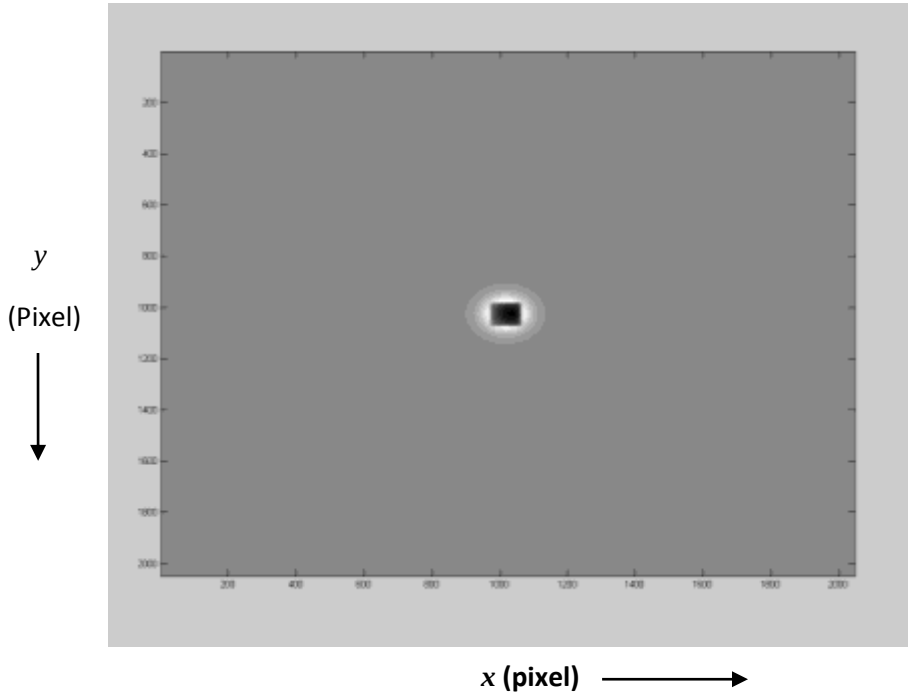


TF(real part) for an ideal CSI

Calibrating lateral scale of CCI

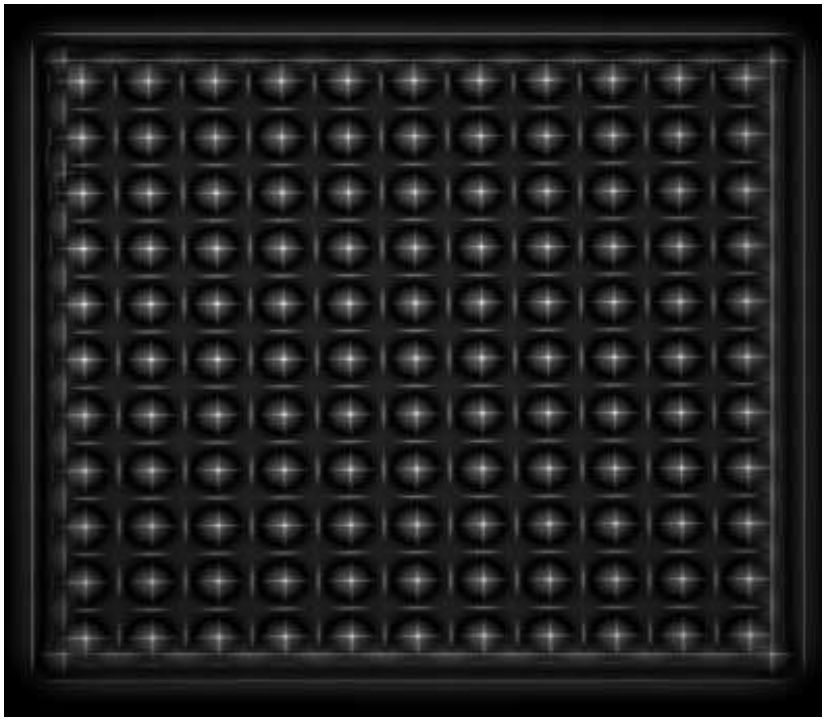


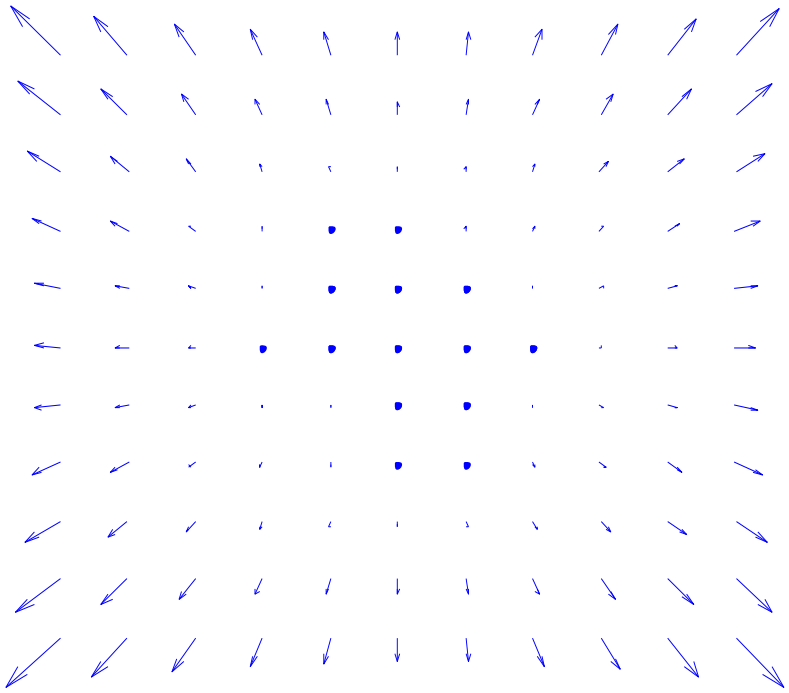
Grid pattern for calibrating lateral scales (real)



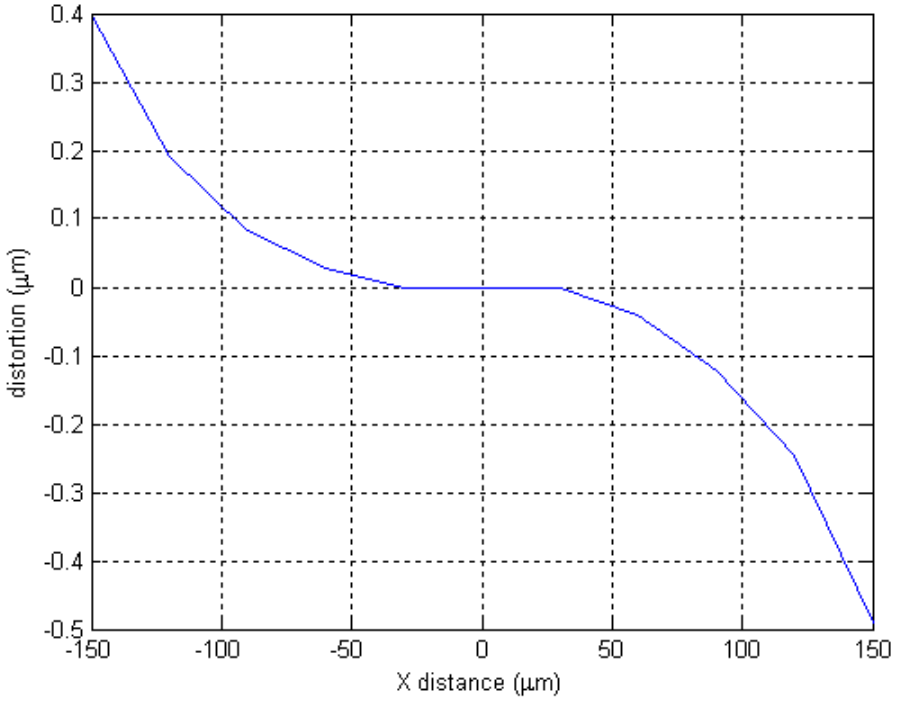
One grid block (real)

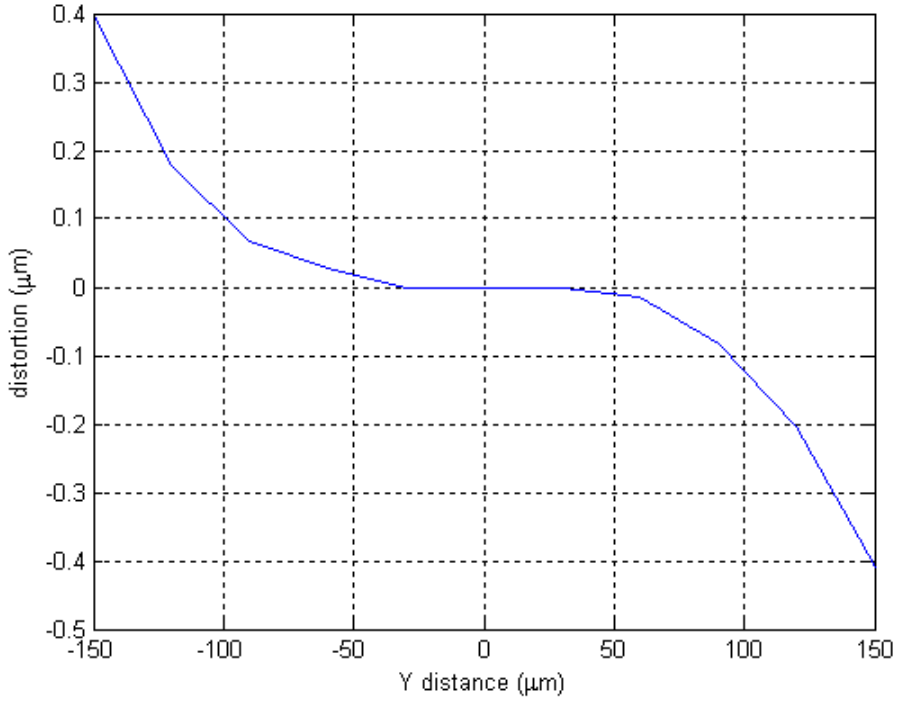
Distortion





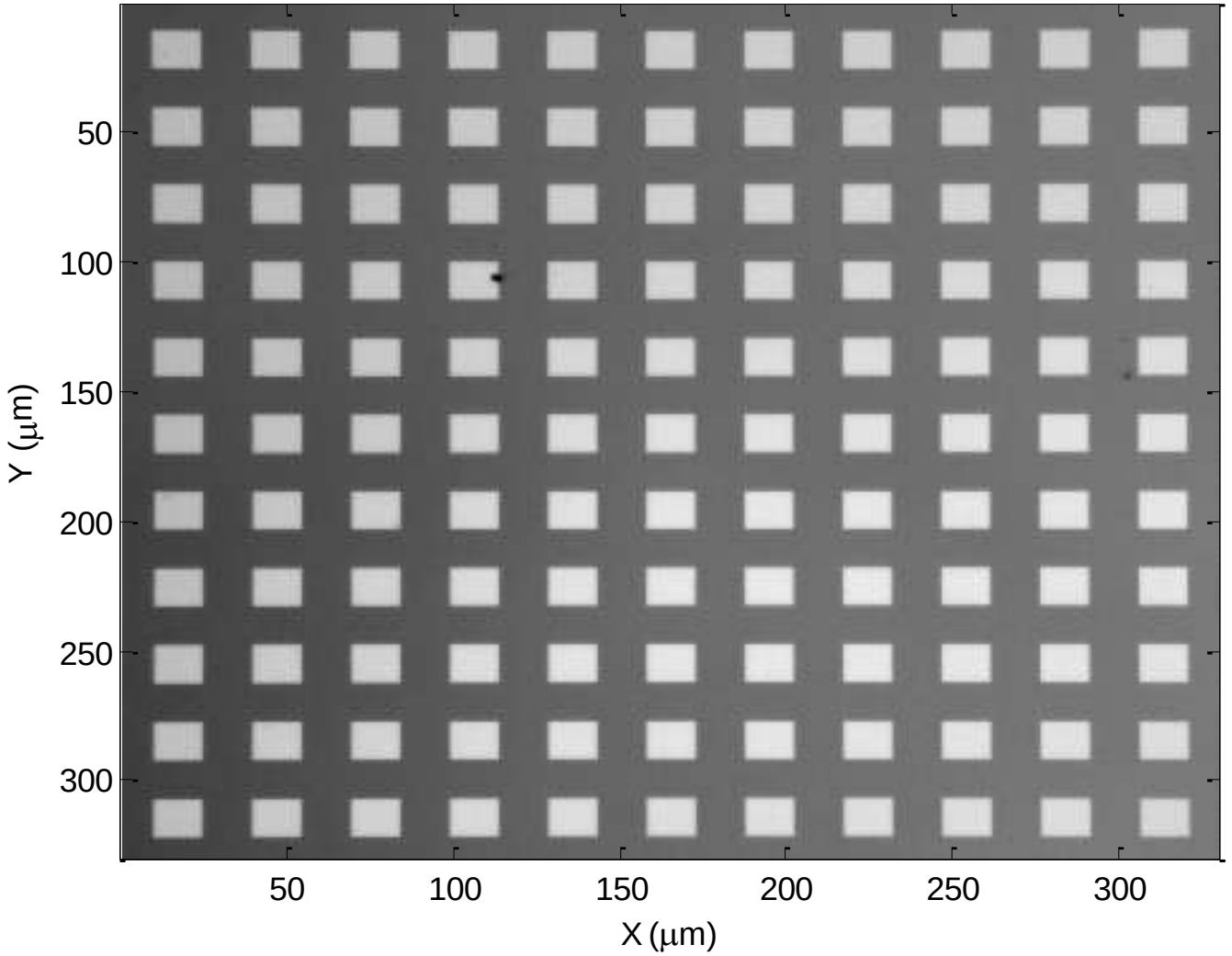
Distortion – 3rd order



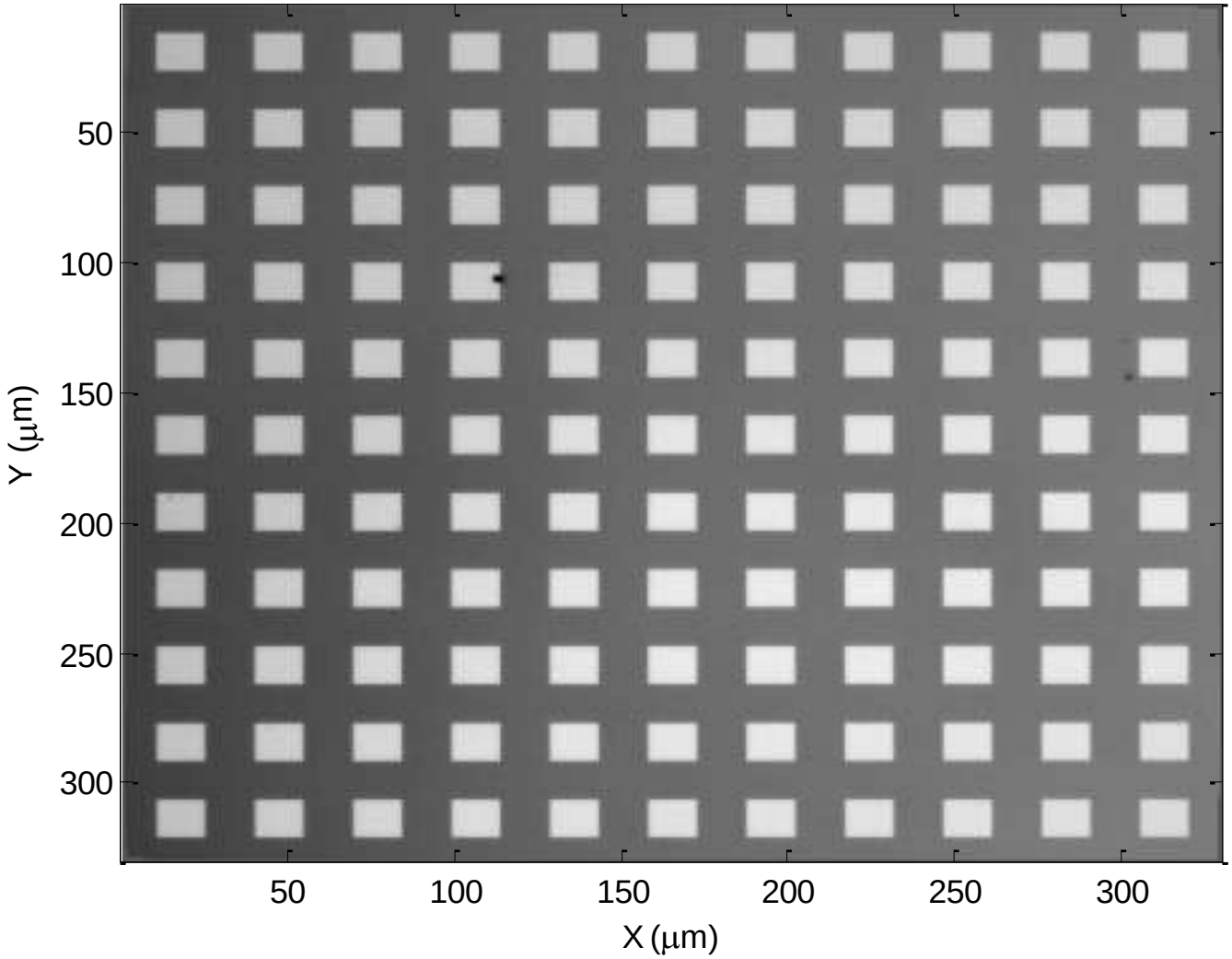


Note: This is the distortion in the raw camera output i.e. the raw fringe data before any correction is applied

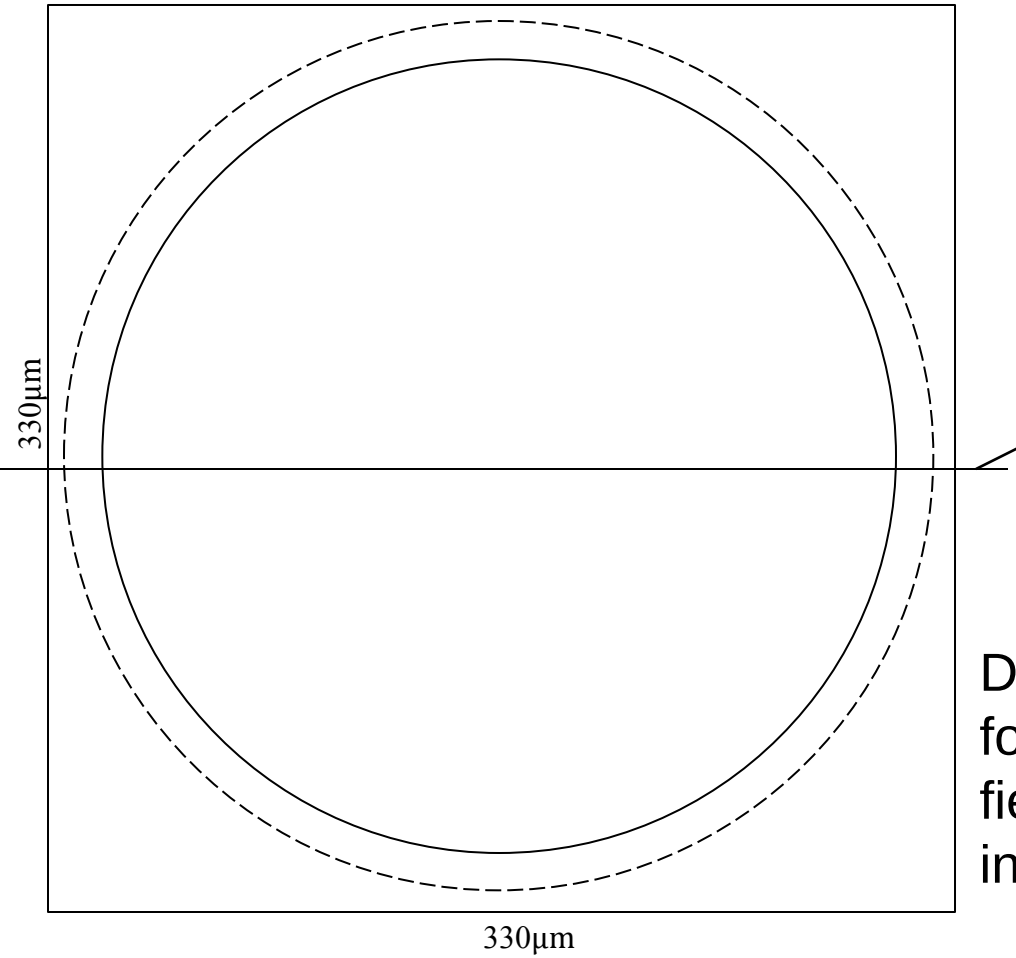
Is it possible to correct for distortion?

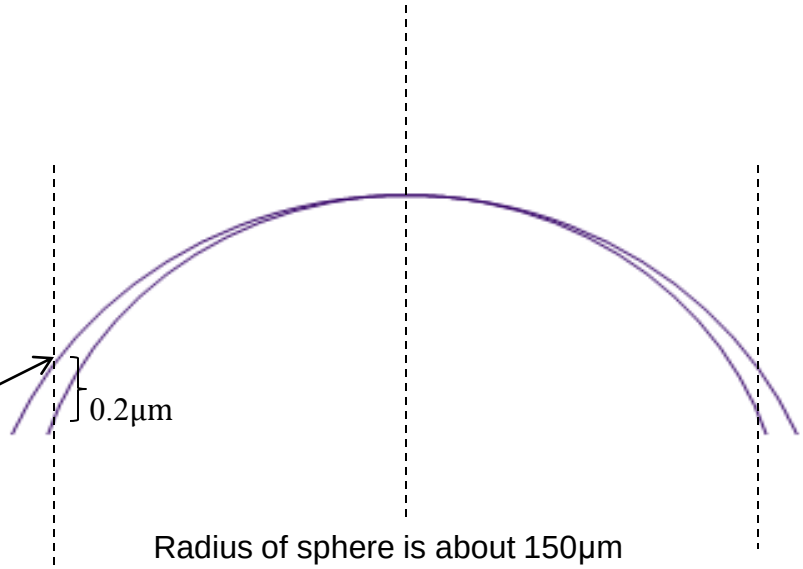


After



Effects of distortion (XYZ)





Distortion varies as (field of view)^3 , for a sphere which cover the whole field of view, an error of 200 nm is introduced at the edges.

PSF measurement

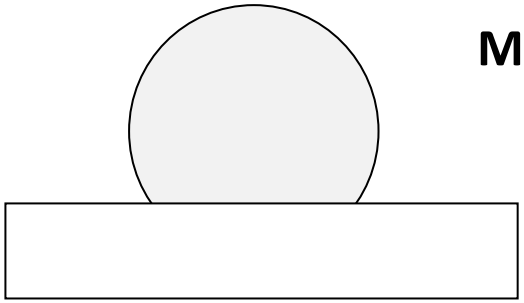
National Physical Laboratory

- Requires sloped artefact
- Foil model of the artefact must cover the spectral region
- Single measurement preferred

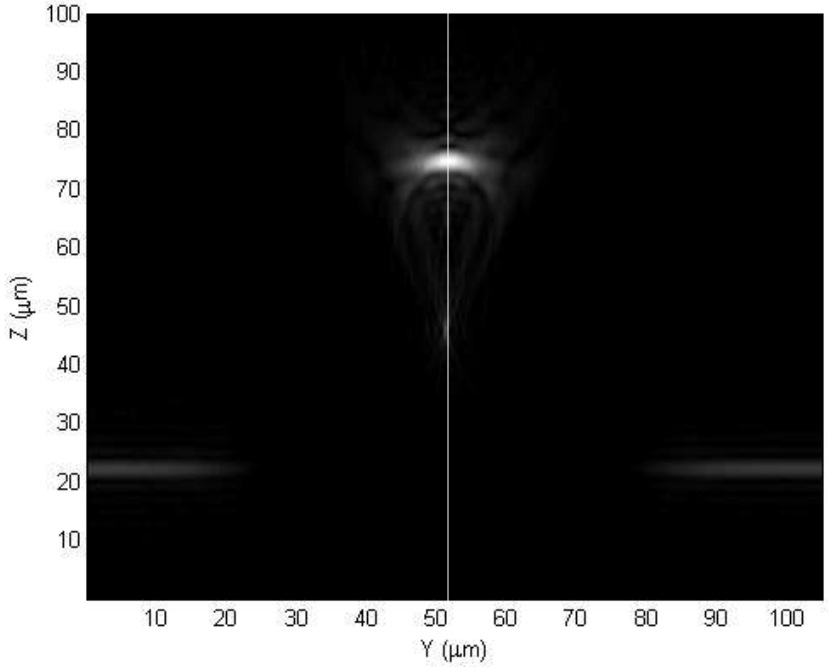
- Spheres!
- Also ball measurement is directly related to lateral resolution $\left(f_{max} = \frac{sin\theta_{max}}{\lambda_{mean}}\right)$

Mercury spheres

- Preliminary measurements were taken using mercury droplets.
  - Mercury droplets of different sizes can be made easily
  - Spherical due to surface tension (pressure ≈ 1 atm.)
  - Surfaces are usually smooth
  - Unknown radius

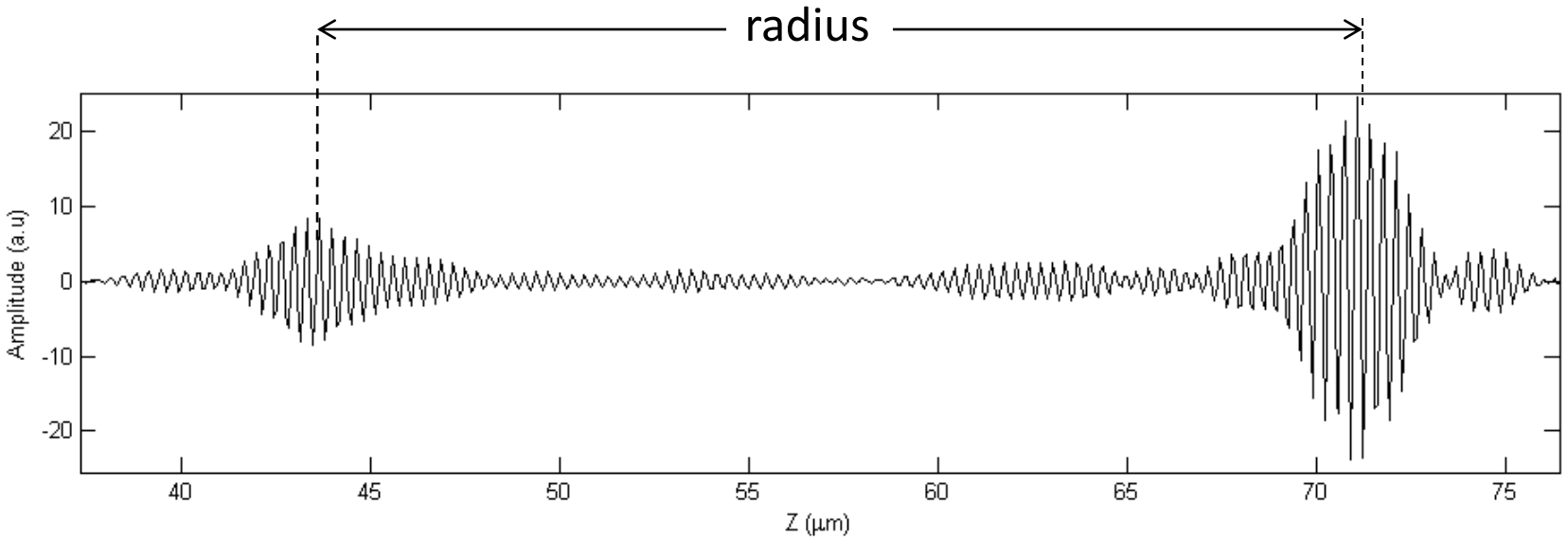


Measurement of radius



Interferogram of a sphere using quasi-monochromatic CSI (absolute part)

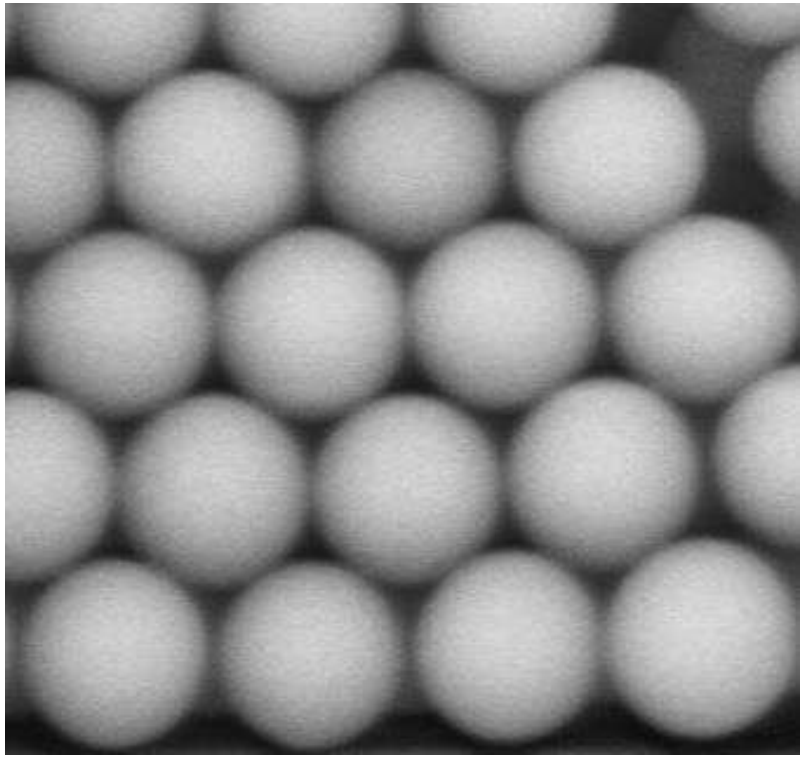
Measurement of radius



The radius was found to be 27.45 µm

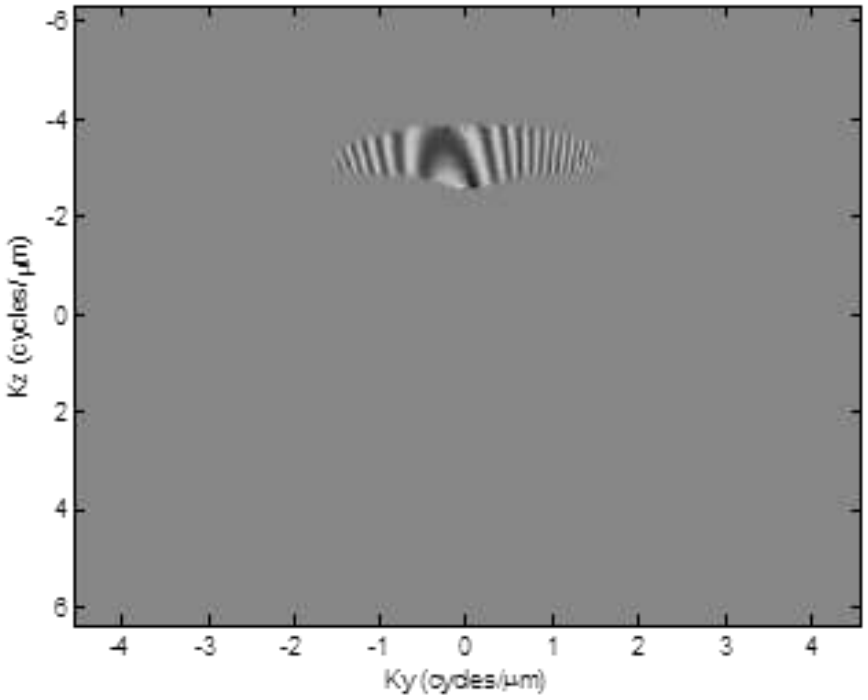
New spheres

- NIST traceable silica microspheres
- Diameter 53.0 ± 1.0 μm
- Alumina also available

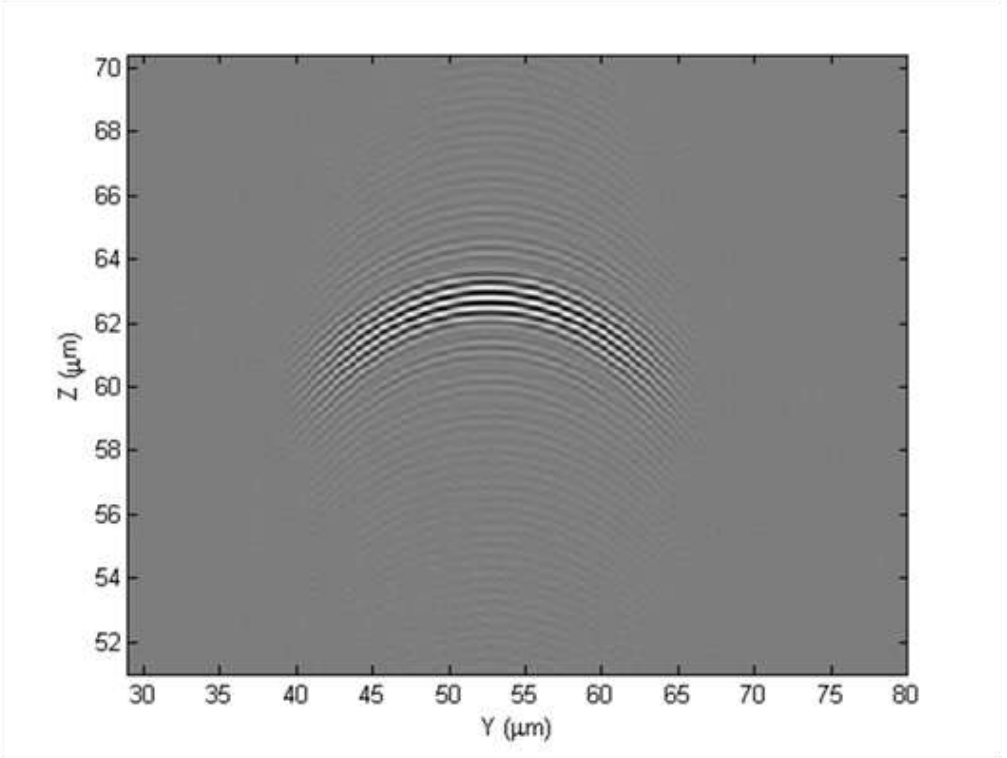


Corrected fringe pattern and spectrum

National Physical Laboratory

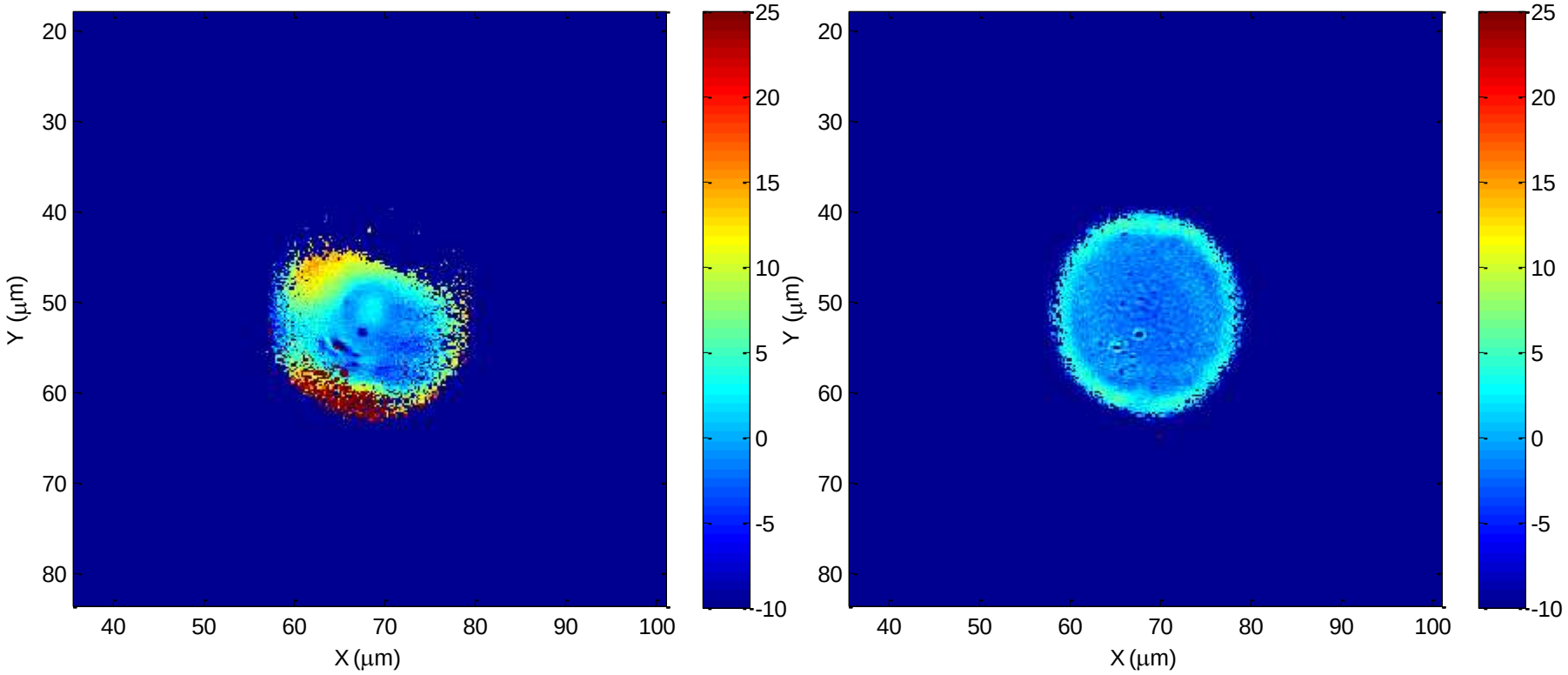


Corresponding spectrum

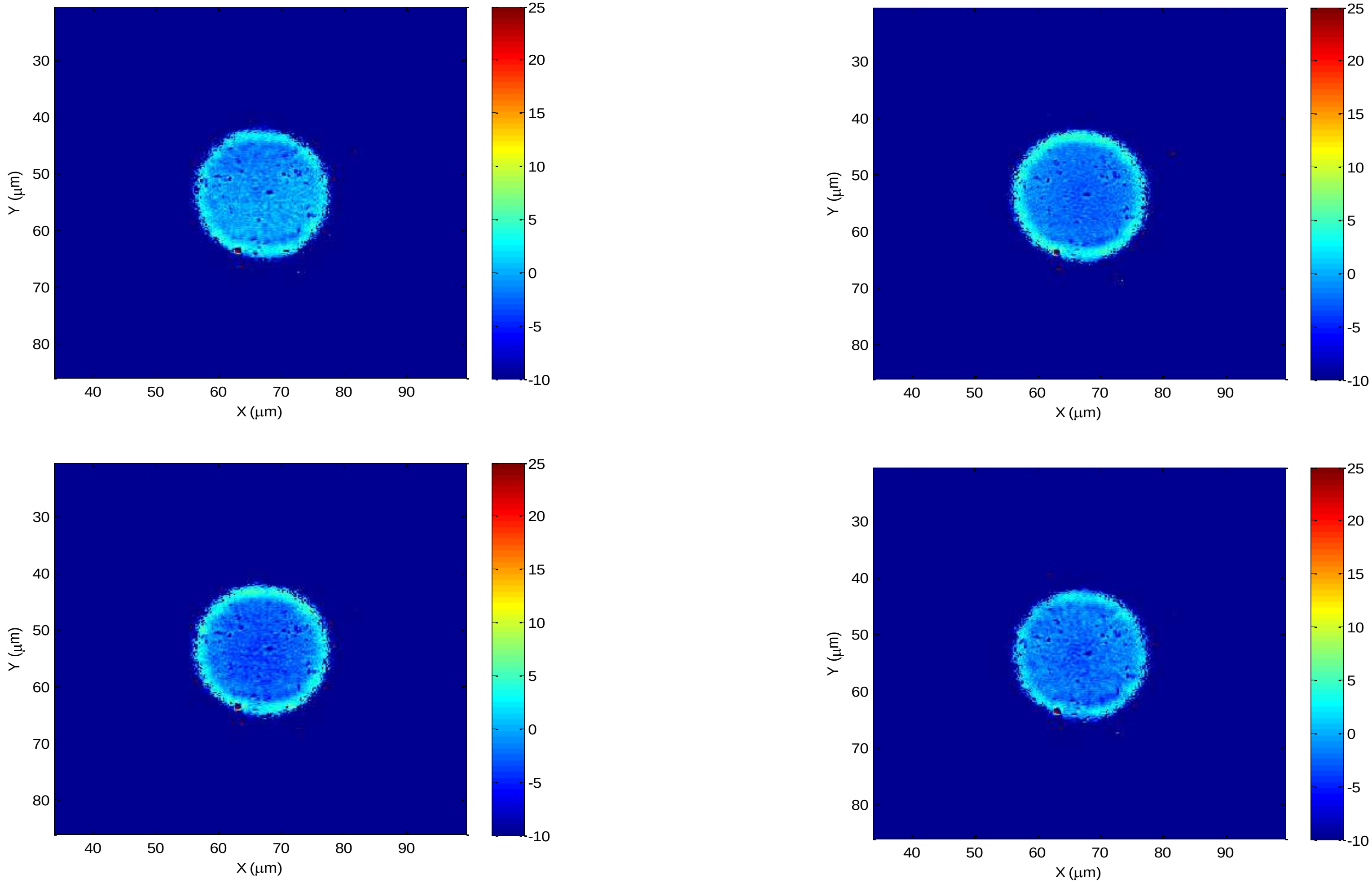


Corrected fringes

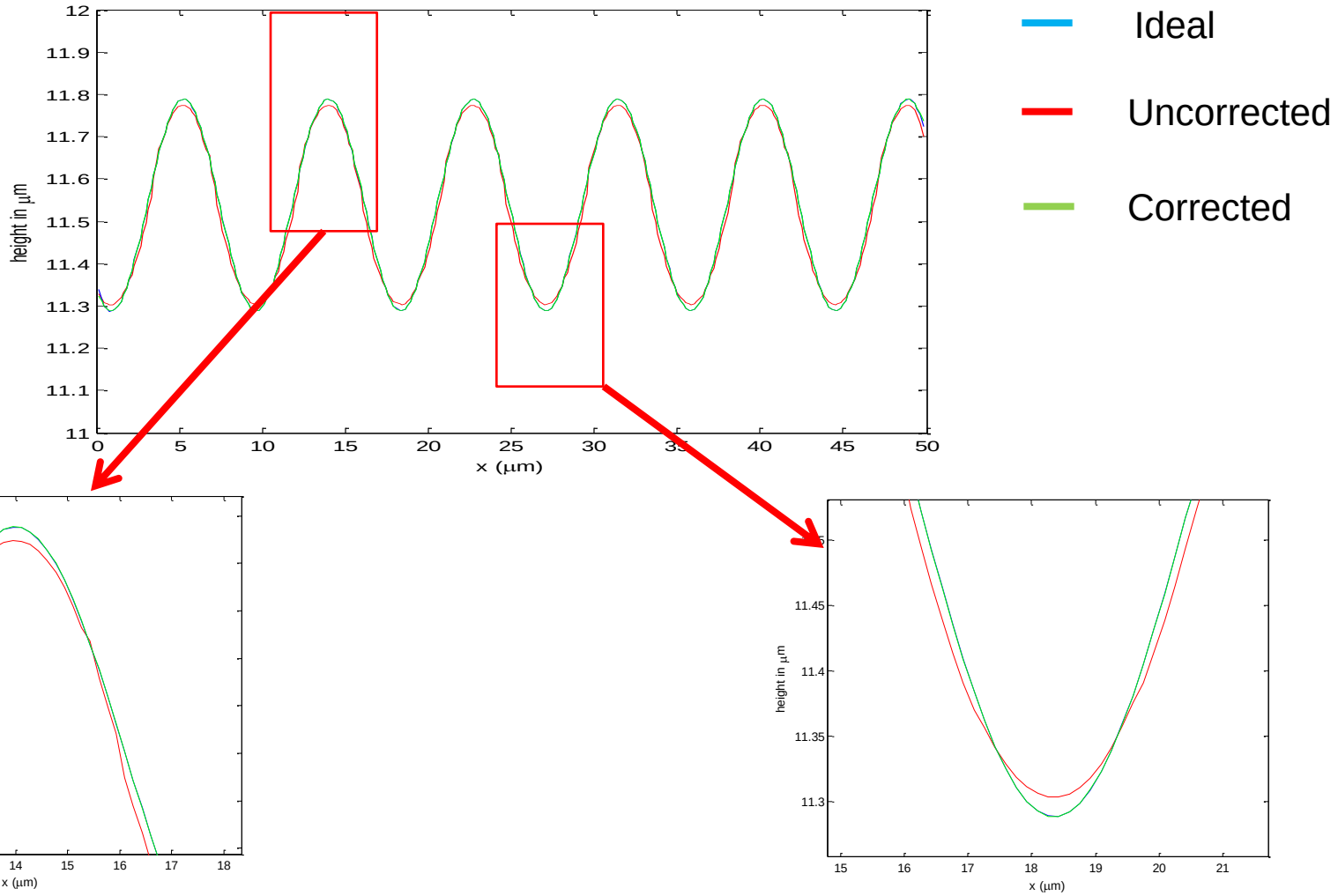
CSI before and after



Repeatability



CCI correction applied to sin(x) foil



Conclusions

- Current CCI instrumentation (50X) exhibits substantial systematic errors

  XY distortion (circa 50 nm System 1, 400 nm System 2)

  Focus (circa 50+ nm both)

  Mirau objective problems (circa 50 nm both)

- We have devised methods of adjustment to compensate

  XY de-warping

  Fringe (inverse) filtering

- It is generally accepted that CSI has nanometre **resolution**. With these methods we can demonstrate nanometre **accuracy**.

Where next with calibration for areal surface metrology?

- Solve 3D inverse problem for CSI (done), confocal (on-going) and focus-variation (not started)

Where next with calibration for areal surface metrology?

- Solve 3D inverse problem for CSI (done), confocal (on-going) and focus-variation (not started)
- Develop calibration methods based on TF

Where next with calibration for areal surface metrology?

- Solve 3D inverse problem for CSI (done), confocal (on-going) and focus-variation (not started)
- Develop calibration methods based on TF
- Develop method for sphere form measurement

Where next with calibration for areal surface metrology?

National Physical Laboratory

- Solve 3D inverse problem for CSI (done), confocal (on-going) and focus-variation (not started)
- Develop calibration methods based on TF
- Develop method for sphere form measurement
- Investigate effects when there are multiple reflections, i.e. linear approximations do not apply

Where next with calibration for areal surface metrology?

National Physical Laboratory

- Solve 3D inverse problem for CSI (done), confocal (on-going) and focus-variation (not started)
- Develop calibration methods based on TF
- Develop method for sphere form measurement
- Investigate effects when there are multiple reflections, i.e. linear approximations do not apply
- Apply methods for ISO standardization

Acknowledgements

- At NPL: Mr Claudiu Giusca
- At Loughborough: Prof Jeremy Coupland, Mr Kanik Palodhi, Mr Rahul Mandal
- At Imperial: Dr Matthew Foreman
- At Taylor Hobson: Dr Danny Mansfield
- At Zygo: Dr Peter de Groot
- At Harbin: Dr Jian Liu

Structured and Freeform Surfaces

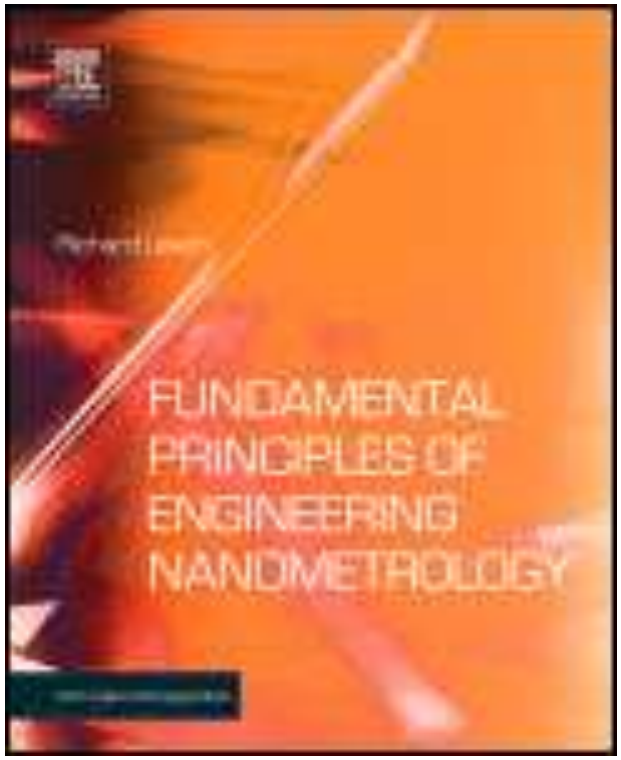
NPL National Physical Laboratory

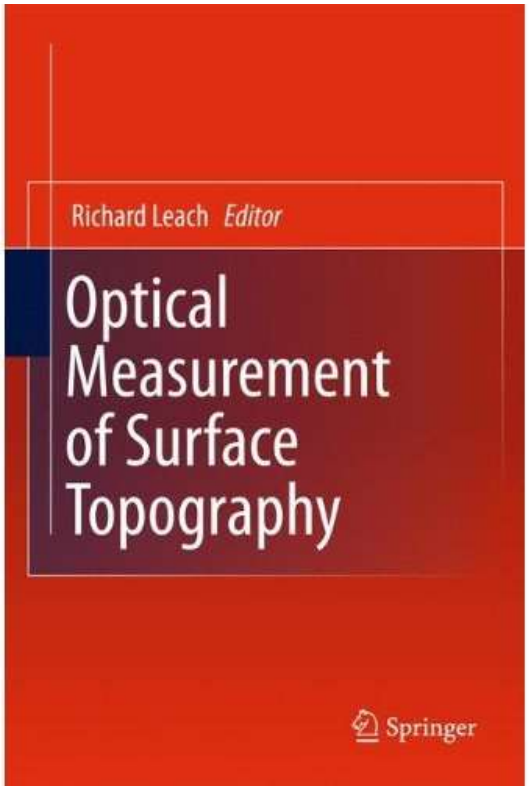
- euspen Topical Meeting
- 5 – 6 December 2012
- National Physical Laboratory (NPL), Teddington, UK
- www.sfs2012.euspen.eu/

Met & Props 2013

- Metrology & Properties of Engineering Surfaces
- 17 – 21 June 2013
- Center for Measurement Standards of the Industrial Technology Research Institute (CMS/ITRI), Taipei, Taiwan
- www.metprops2013.itri.org.tw

NPL
National Physical Laboratory





4th Target Fabrication Workshop
Mainz, Germany
19-23 August 2012

P.N.Lebedev Physical Institute of the Russian Academy of Sciences

University of St Andrews

X-Ray Tomography Method for Characterization of Aerogel Targets with Density Gradient

N.G.Borisenko[2], W. Nazarov [1], Christopher Musgrave [1], Yu.A. Merkuliev [2], ***Andrey Orekhov[2]***, L.A. Borisenko [2,3]

[1] St. Andrews University, North Haugh, St. Andrews, Scotland

[2]P.N.Lebedev Physical institute RAS, Moscow, Russia

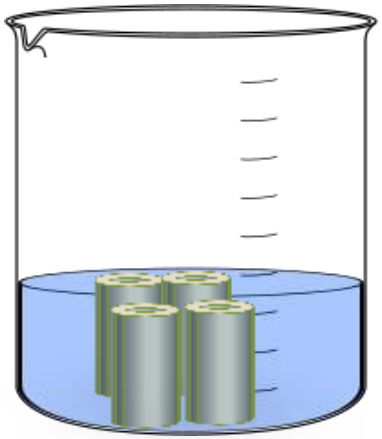
[3]M.V. Lomonosov Moscow State University, Moscow, Russia

Low-density materials

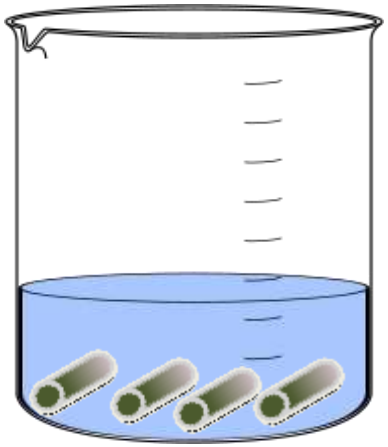
in laser targets are interesting for

- Increased light absorption in low-density layer
- Smoothing of laser light on target surface
- Among them: Density gradient targets or stepwise-density layers were considered in experimental and theoretical papers on astrophysics modelling, equation-of-state and shock wave dynamics research.
- We consider below polymer aerogel with density gradient synthesized in University of St. Andrews

One-step Synthesis of Gradient Density Polystyrene Aerogels



1. Small diameter tubes placed in solvent, monomer and Lewis acid catalyst solution



2. After polymerisation completed, tubes placed in methanol for solvent exchange

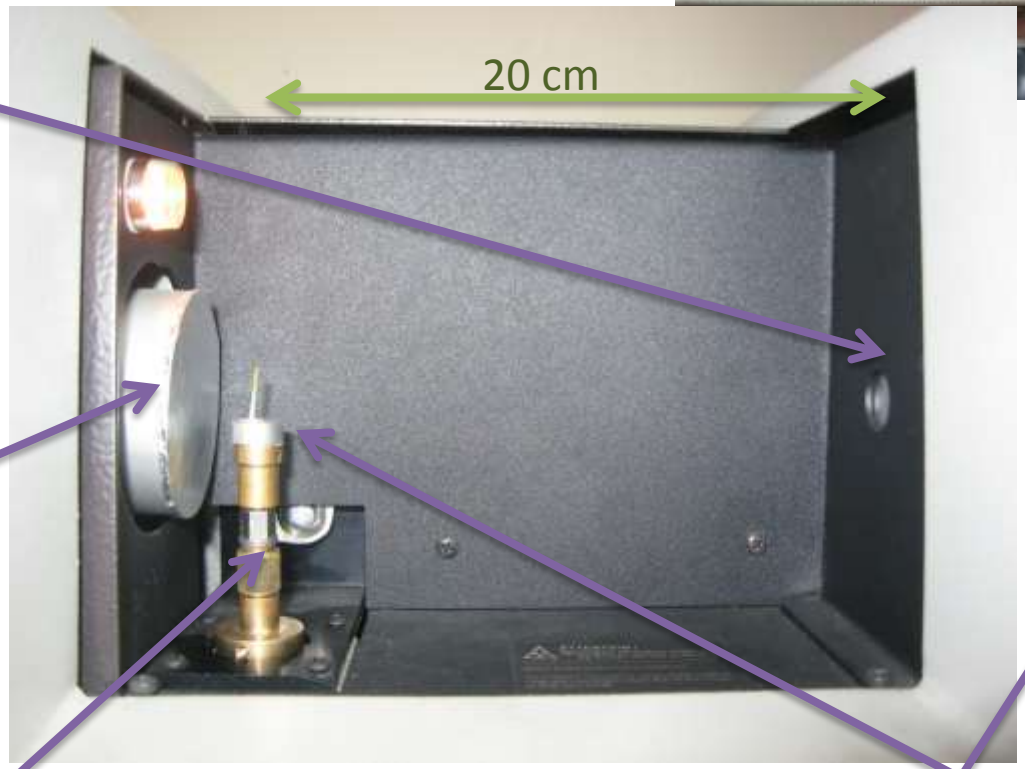
3. After solvent exchange is complete, samples are transferred into a **Polaron®** Critical Point Dryer, for solvent removal

Low Density region High Density region

Dried Gradient Density Foam

Skyscan 1074
Micro CT scanner

X-ray tube window
- U=20-40 kV
- A_{max}=1000 µA
- Ø = 100 µm

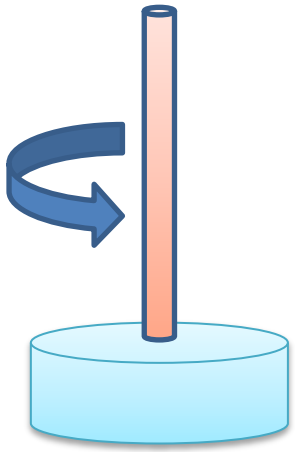


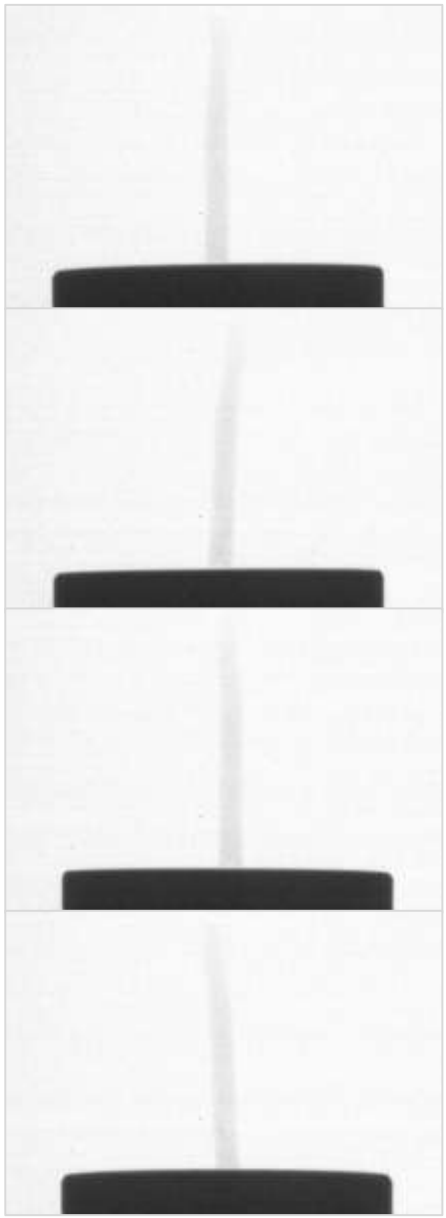
CCD-camera looking at phosphor screen under thin Al filter
- Pixel size 21 µm
- 12 bit depth

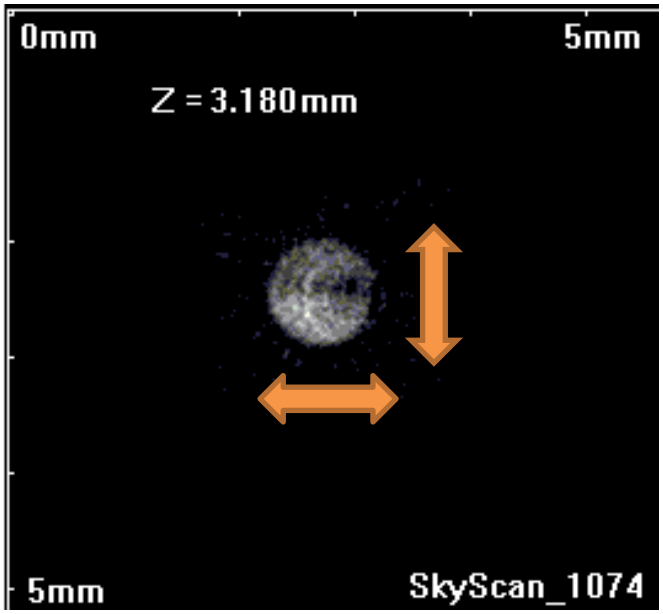
Rotating table for samples. Minimum rotating angle – 0.9° (400 steps per 1 turn)

Polystyrene foam sample, mounted on Al washer

Density measurements







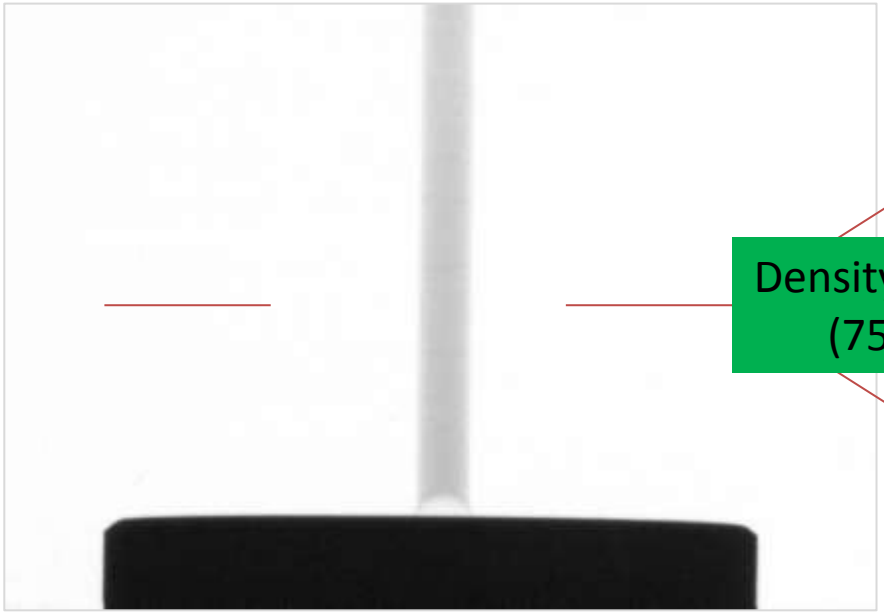
$$I = I_0 \cdot e^{-\mu \cdot t}$$

μ [μm^{-1}] – absorption ratio

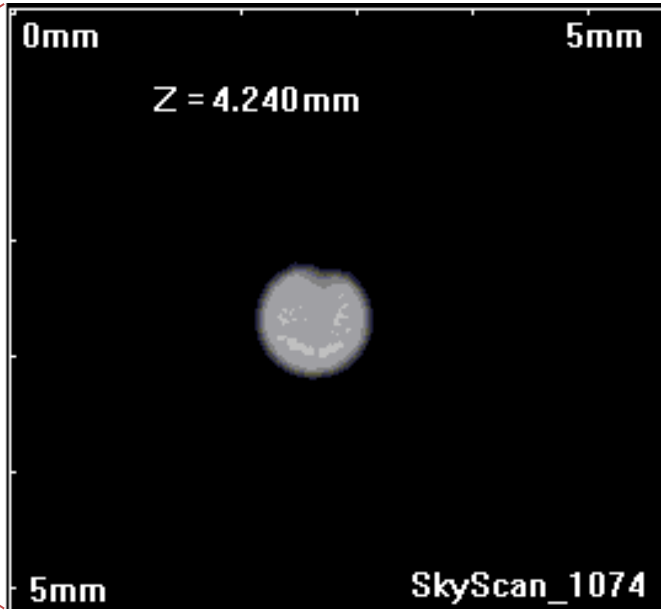
$$t = \frac{\rho}{\rho_{solid}} \cdot x$$

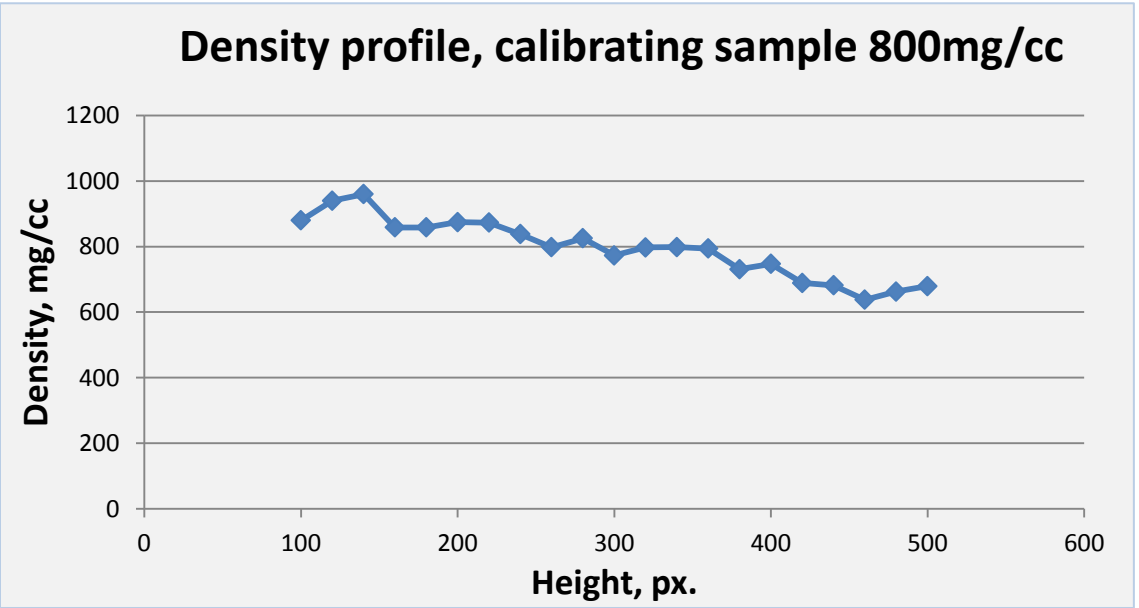
x [μm] – absorption thickness

Calibration sample



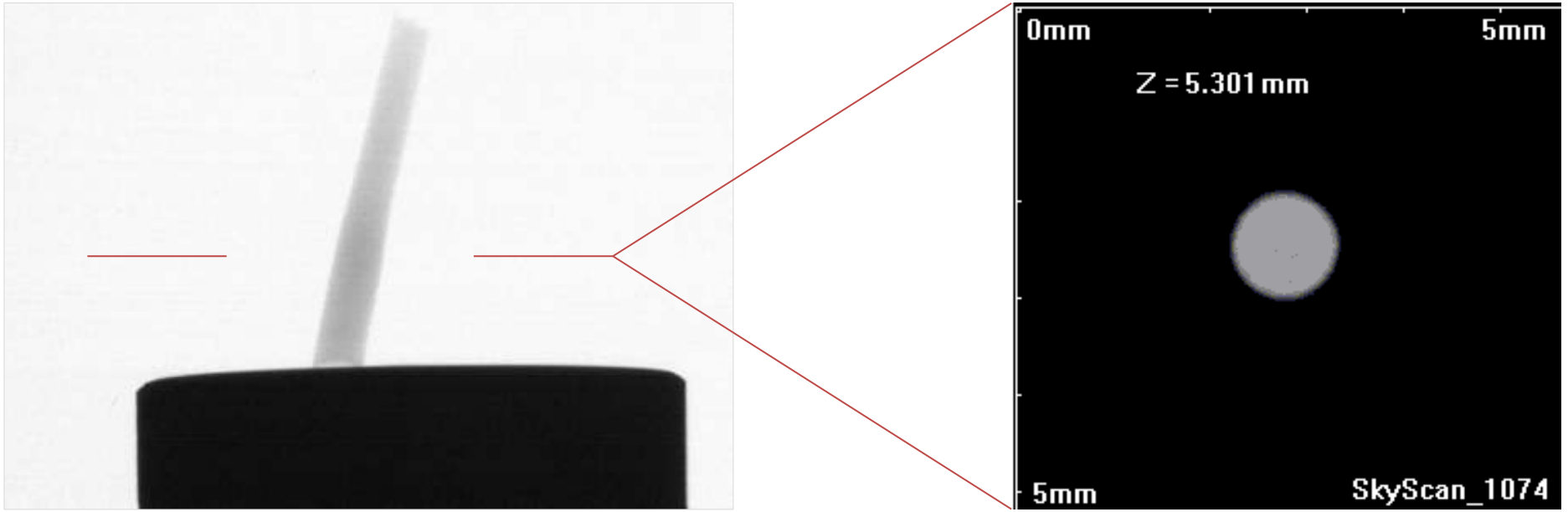
Density 800 mg/cc
(75% solid)

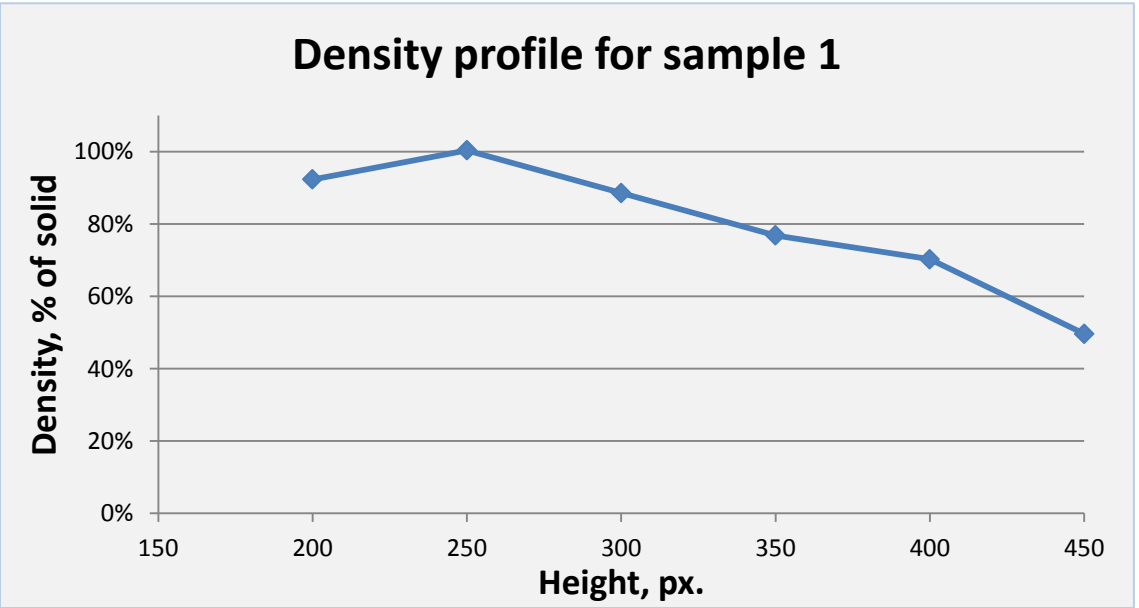




Height from the bottom of frame	Thickness measured, um +-20
200 px (4 mm)	955
250 px (5 mm)	955
300 px (6 mm)	955
350 px (7 mm)	955
400 px (8 mm)	955
450 px (9 mm)	955

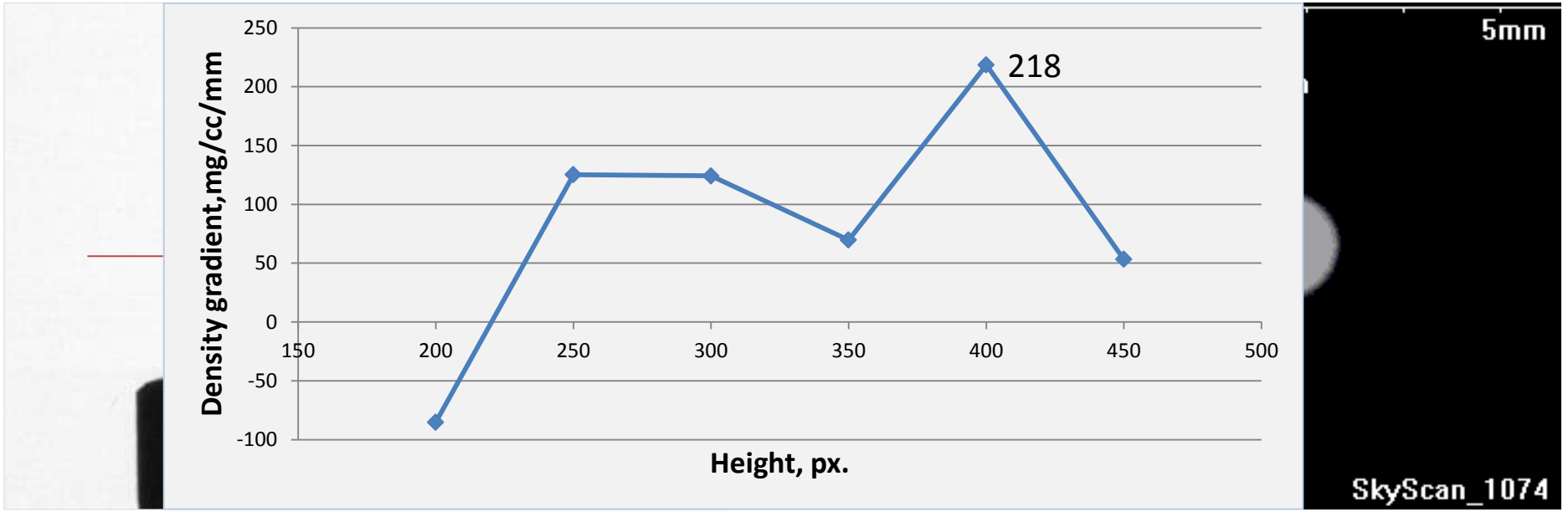
Sample #1 (“typical”)

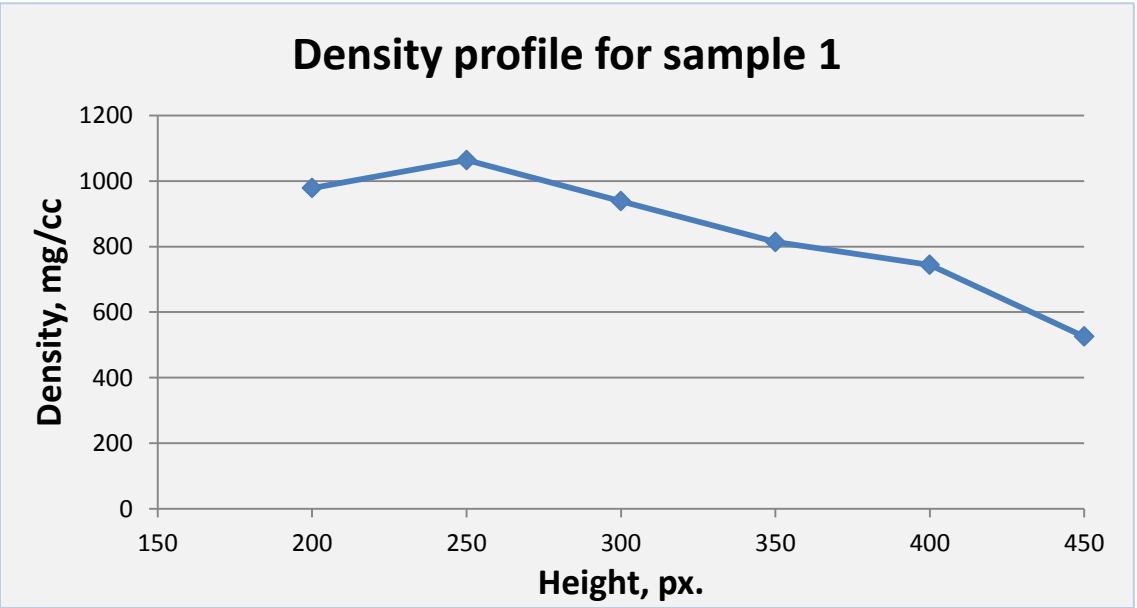




Height from the bottom of frame	Thickness measured, um +-20
200 px (4 mm)	1105
250 px (5 mm)	1040
300 px (6 mm)	955
350 px (7 mm)	920
400 px (8 mm)	875
450 px (9 mm)	875

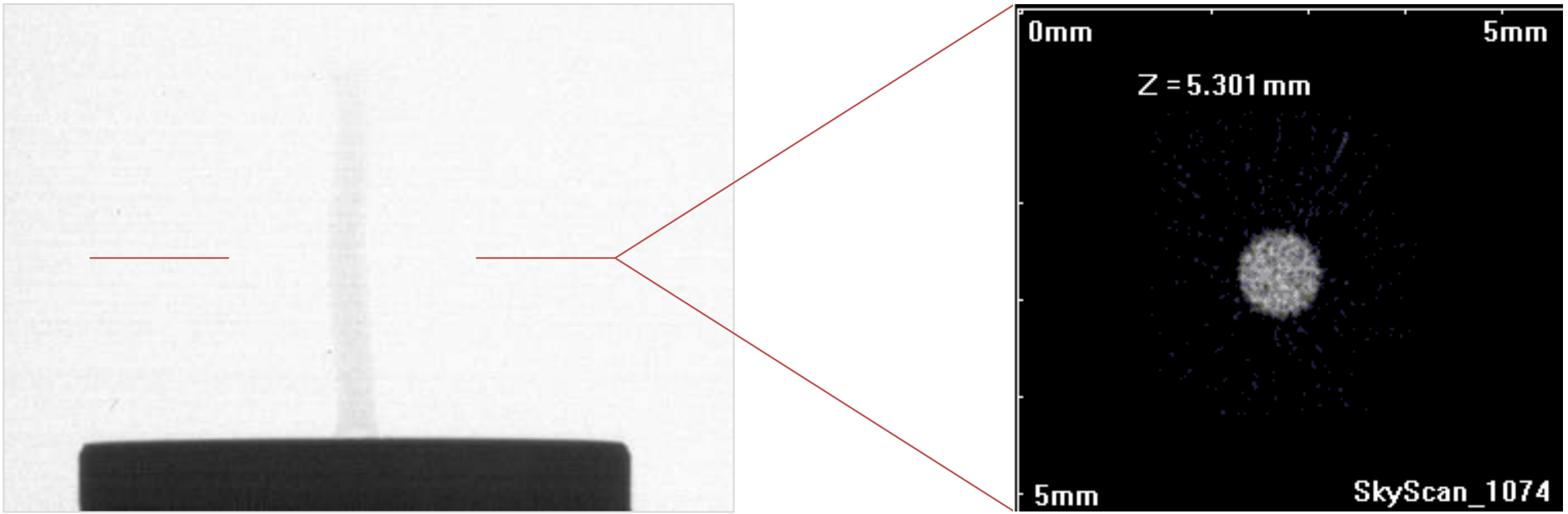
Sample #1 (“typical”)

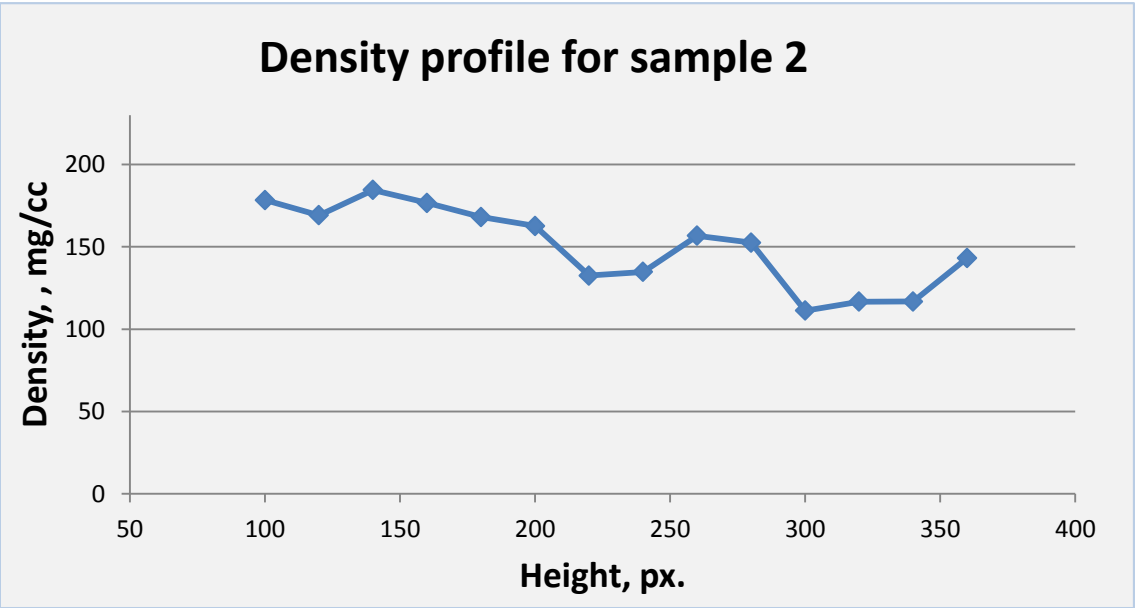




Height from the bottom of frame	Thickness measured, um +-20
200 px (4 mm)	1105
250 px (5 mm)	1040
300 px (6 mm)	955
350 px (7 mm)	920
400 px (8 mm)	875
450 px (9 mm)	875

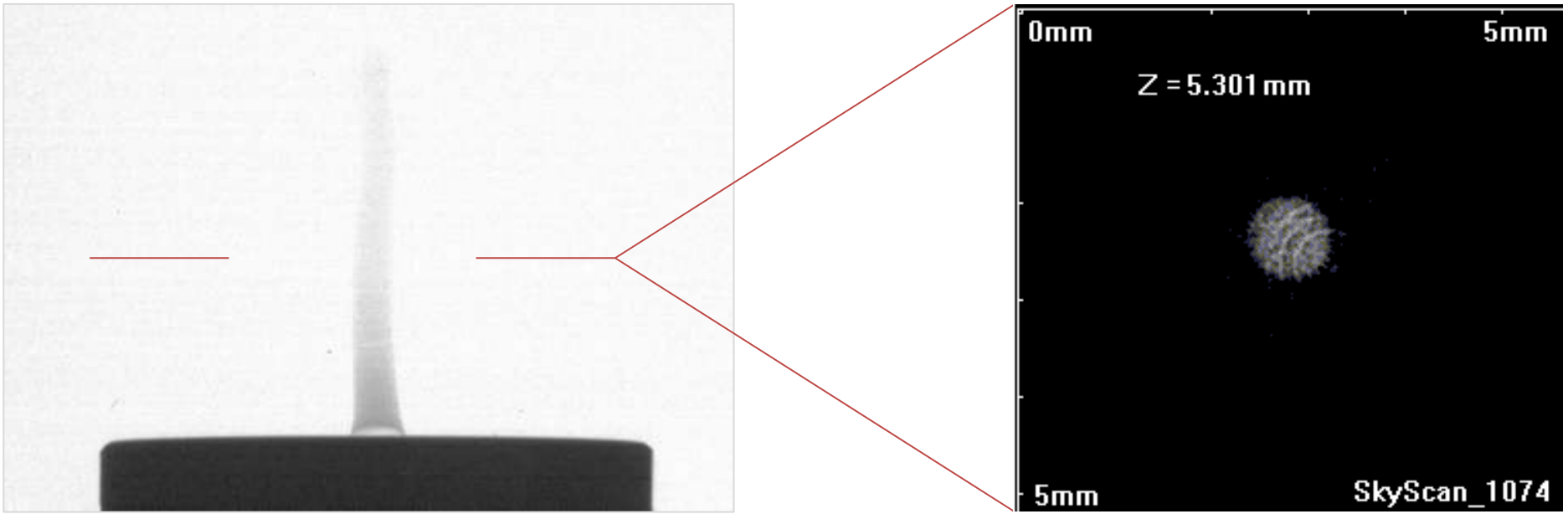
Sample #2 (“fluctuating”)

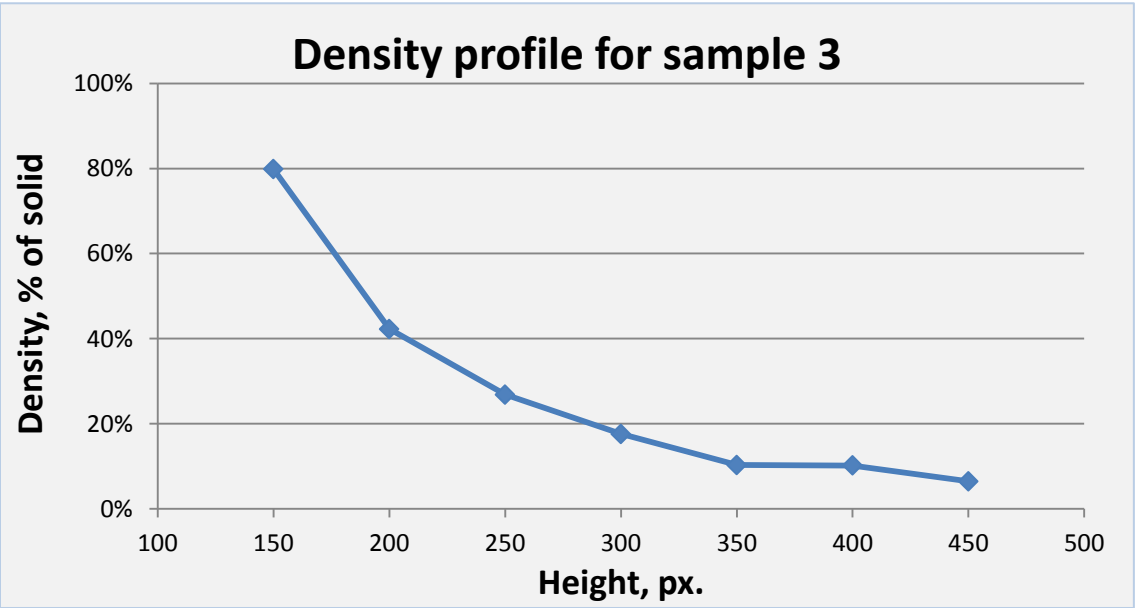




Height from the bottom of frame	Thickness measured, µm +-20
100 px (2 mm)	895
150 px (3 mm)	840
200 px (4 mm)	895
250 px (5 mm)	870
300 px (6 mm)	830
350 px (7 mm)	765

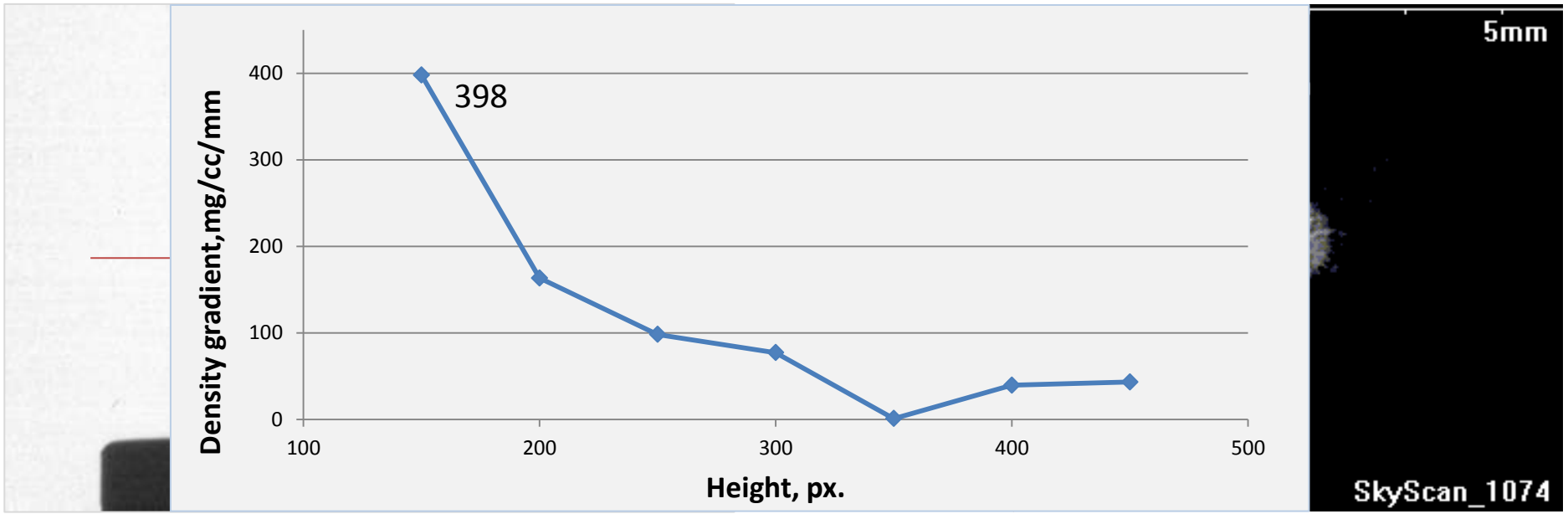
Sample #3 (“good”)

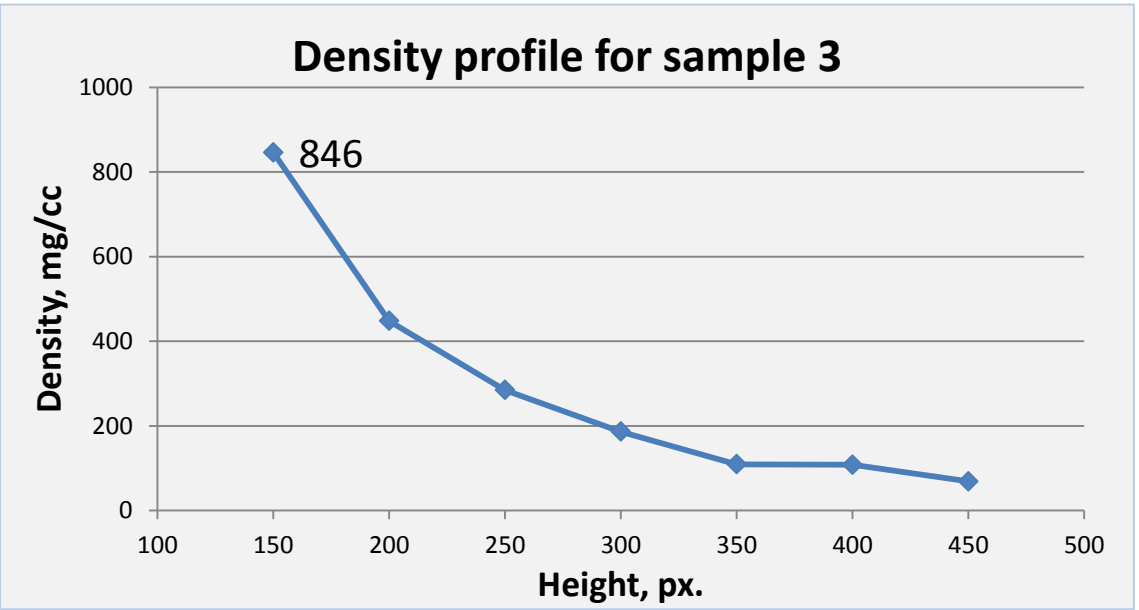




Height from the bottom of frame	Thickness measured, µm +-20
100 px (2 mm)	915
150 px (3 mm)	895
200 px (4 mm)	835
250 px (5 mm)	770
300 px (6 mm)	750
350 px (7 mm)	730

Sample #3 (“good”)





Height from the bottom of frame	Thickness measured, µm +-20
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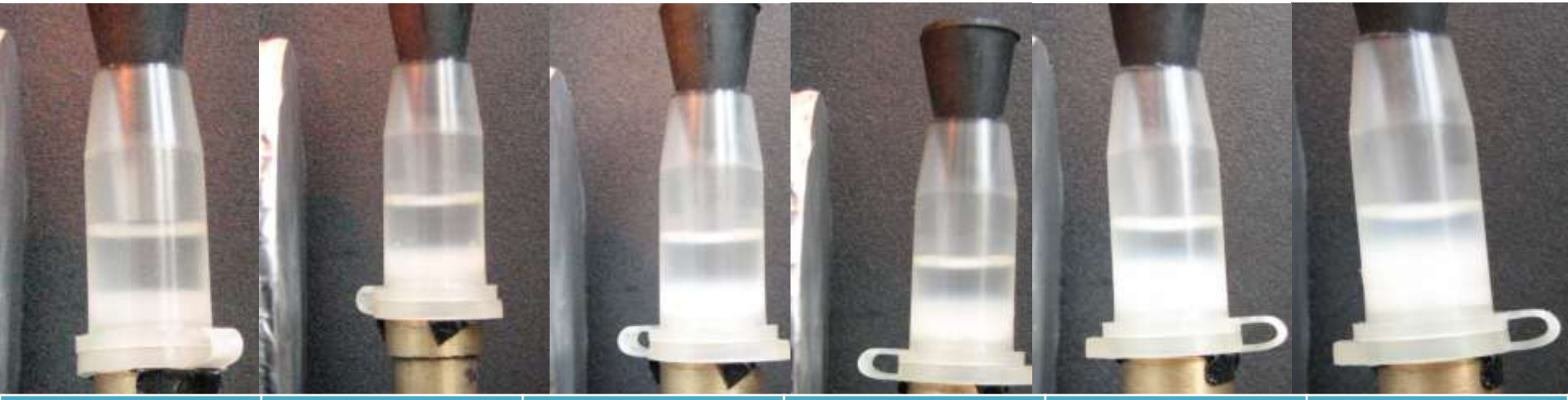
350 px (7 mm)	730

Characterization results

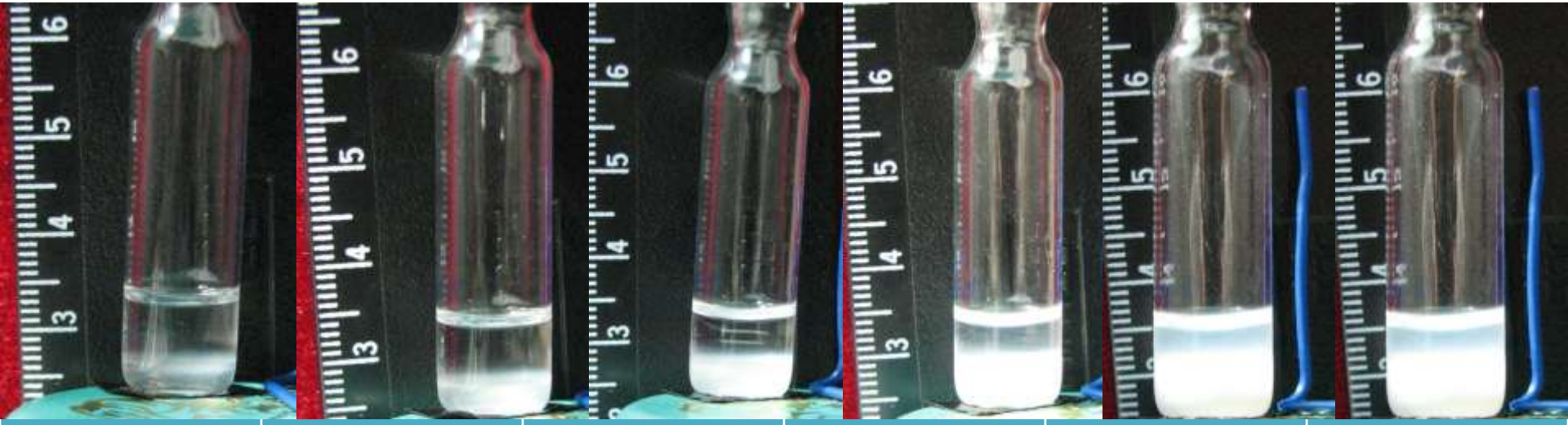
- The method is capable of observation of polymer aerogel samples (mm-scale)
- Measurements proved the density gradient to be produced by proposed synthesis technique
- Dry samples were measured to demonstrate up to 400 mg/cm^3/mm gradient along the cylinder axis
- Good samples have uniform cross-sections all over the height

Further development is needed for repeatability and to reach desired gradients

Wet silica gel density gradient formed and observed during synthesis

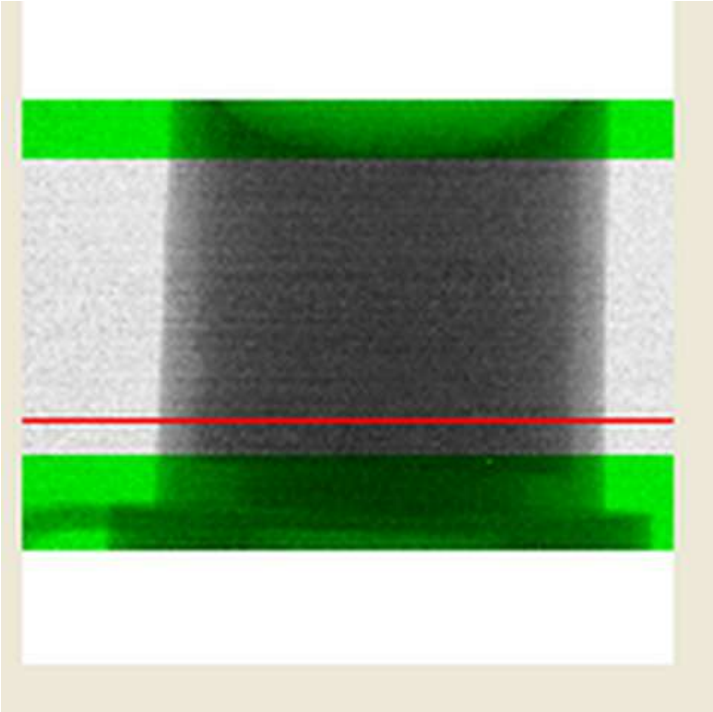


7 min	21 min	55 min	93 min	124 min	200 min

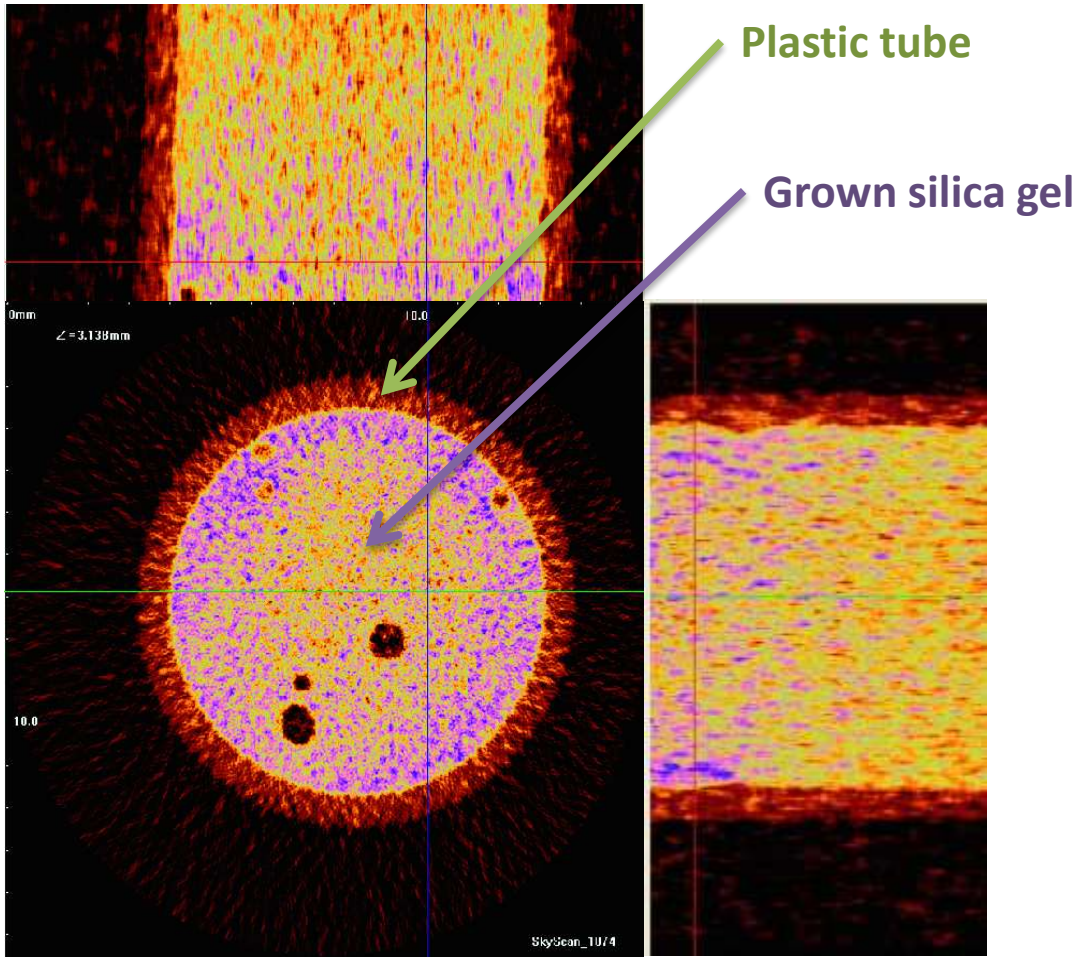


9 min	18 min	40 min	99 min	125 min	260 min

Sample from plastic tube

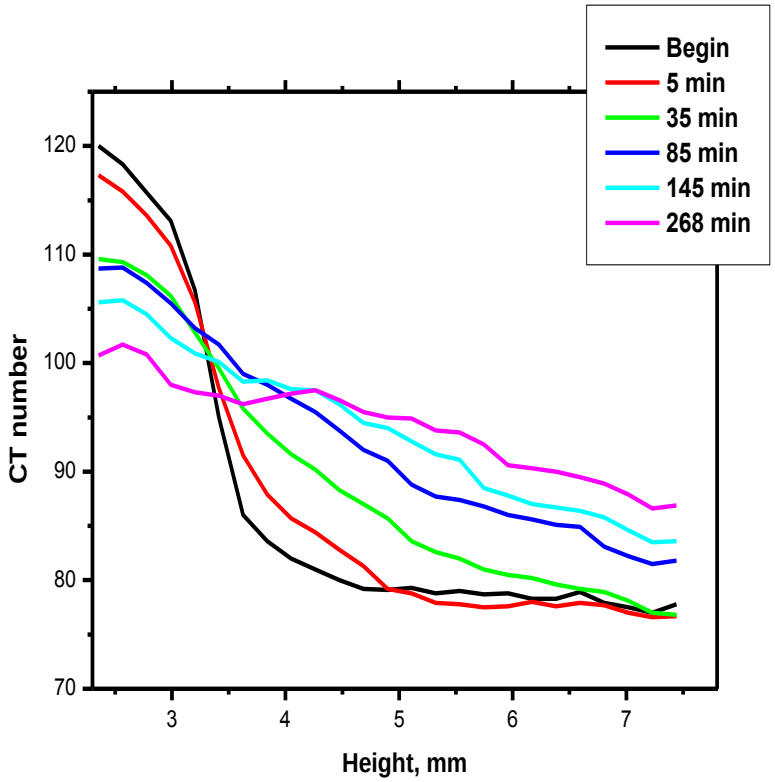


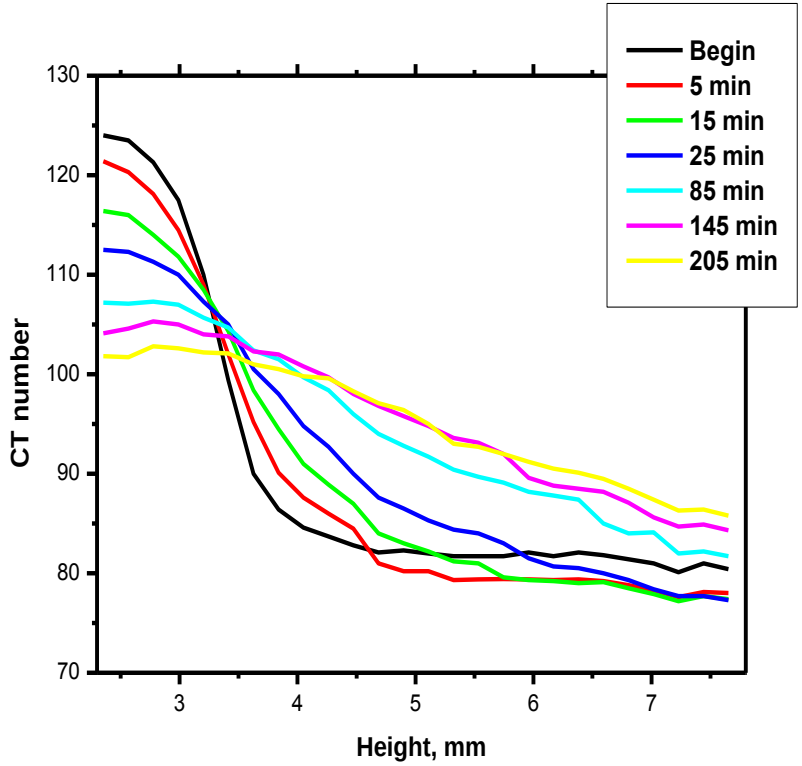
X-ray image, green areas are excluded from analysis



Usual view of silicagel growth on x-ray tomography after reconstruction

Dependence of growing SiO_2 concentration via height





Dependences of count tomography numbers on height of the tube during gel growth at various time for two starting concentrations: left – 0.167 basic solution, right – 0.125 basic solution. (calibration depends on time)

Referrence: *X-ray tomography of growing silica gel with a density gradient.* N. Borisenko et al. Fusion Science and Technology, Vol 55, May 2009

Method can be used for

- Non-dried samples measurements
- Real time monitoring during production
- Real time production technology development
- Samples characterization after development after critical point drying

✓ This method is non-destructive. Samples can be used after characterization (as opposed to SEM).

Disadvantages:

—problems with extra-low density

—foams of low-Z elements are too transparent

Conclusion

- One step aerogels with density gradient are demonstrated
- Density gradient is up to 400 mg/cm^3/mm
- Further material development could be supported by x-ray microtomography

Thank you for your attention

Time Domain Nuclear Magnetic Resonance (TD-NMR) as a Novel Tool for the Characterization of Low Density Porous Materials.

Christopher Musgrave[1], Wigen Nazarov[1], Kimberley Anderson[2], Nick Bazin[3], Simon Pitts[3], Lyn Kent[3] and Douglas Faith[3].

[1] University of St Andrews, Unit 4, High Energy Laser Materials Laboratory, North Haugh, St Andrews, Fife, KY16 9ST, UK.

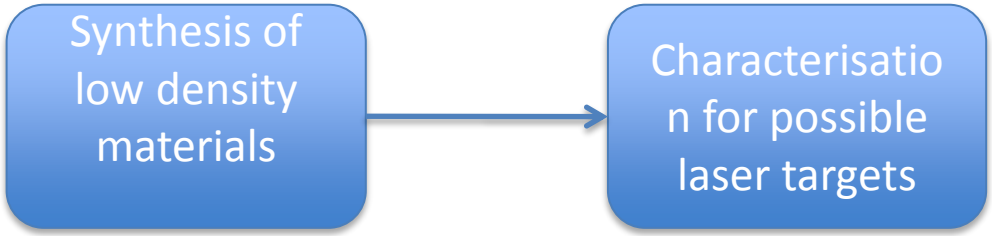
[2] Department of Pure & Applied Chemistry, University of Strathclyde Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, UK.

[3] Atomic Weapons Establishment, Reading, RG7 6DP, UK.

University of St Andrews

Research aims

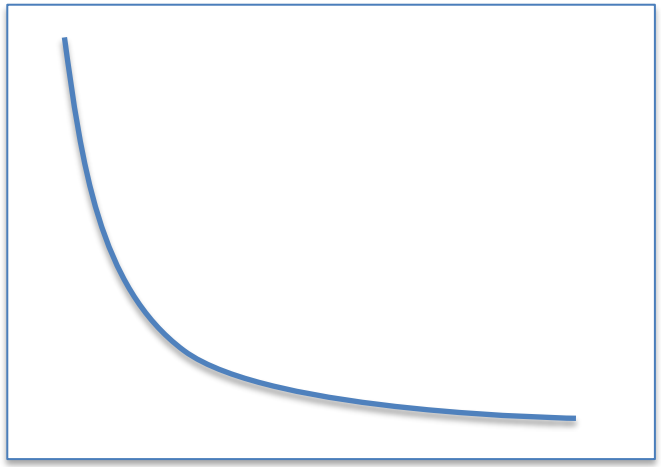
- Synthesis of low density polymeric materials for possible use in plasma physics experiments.



- Characterisation of materials; understanding the structure of the synthesised materials.

Overview

- What is relaxation?
  - NMR relaxation
  - Background of NMR relaxation
- Relaxation;
  - Spin-lattice relaxation.
  - Spin-spin relaxation.
  - Relaxation under Radio Frequency (RF).



- Motions in polymers and relaxation
- Examples
- Summary

Time Domain-Nuclear Magnetic Resonance (TD-NMR)

- TD-NMR, focuses on the NMR signal in the time domain- there is no spectrum- to obtain relaxation times.

- 0.47 T (20 MHz, ^{1}H) magnet with variable temperature system (-100°C to +200°C).
- Solid and liquid samples.
- ^{1}H nuclei observed (I = ½).

Figure 1. TD-NMR system in St Andrews, Scotland.

What is relaxation?

- Investigating the effect of a perturbed system back to an equilibrium state.

- More than one way to relax;
  - Dielectric relaxation (related to electrical conductivity of a material).
  - Structural relaxation of an amorphous material (thermally induced molecular motion).
  - NMR (magnetic) relaxation (intrinsic spin of magnetic nuclei).

- NMR relaxation
  - Restoration of perturbed spins (magnetisation offset vector) back to an equilibrium state.

Relaxation; principles

- The magnetisation offset vector, $\mathbf{M}_0$, (bulk magnetisation) arises from the population difference of up and down spin orientations, given by the Boltzmann distribution.

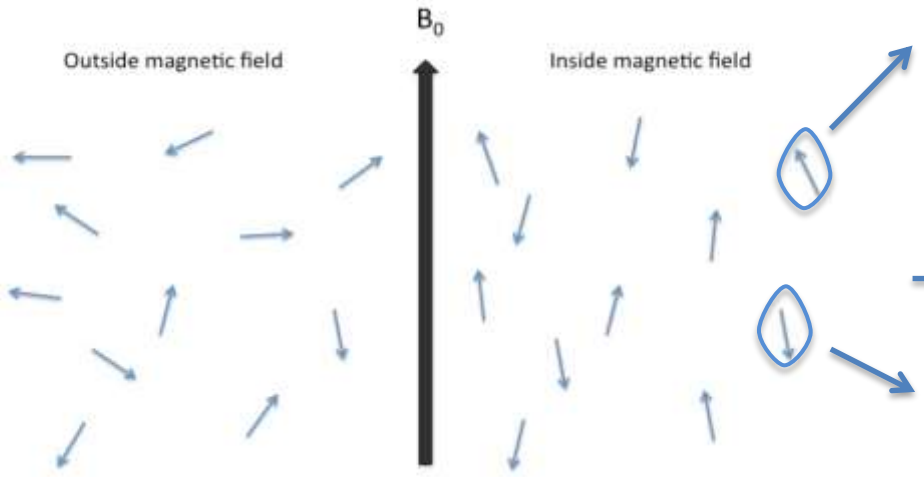


Figure 2. Nuclear spins outside magnetic field (left) and inside magnetic field (right).

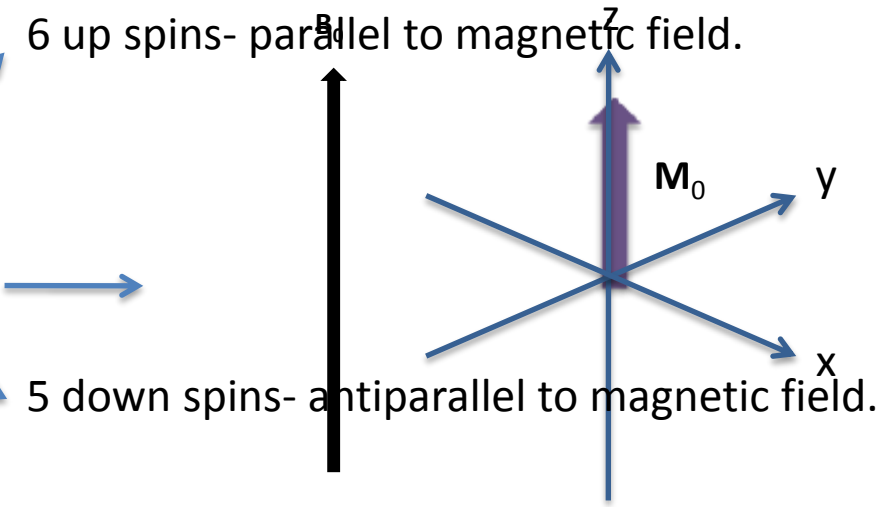


Figure 3. Magnetisation offset vector aligned to external magnetic field.

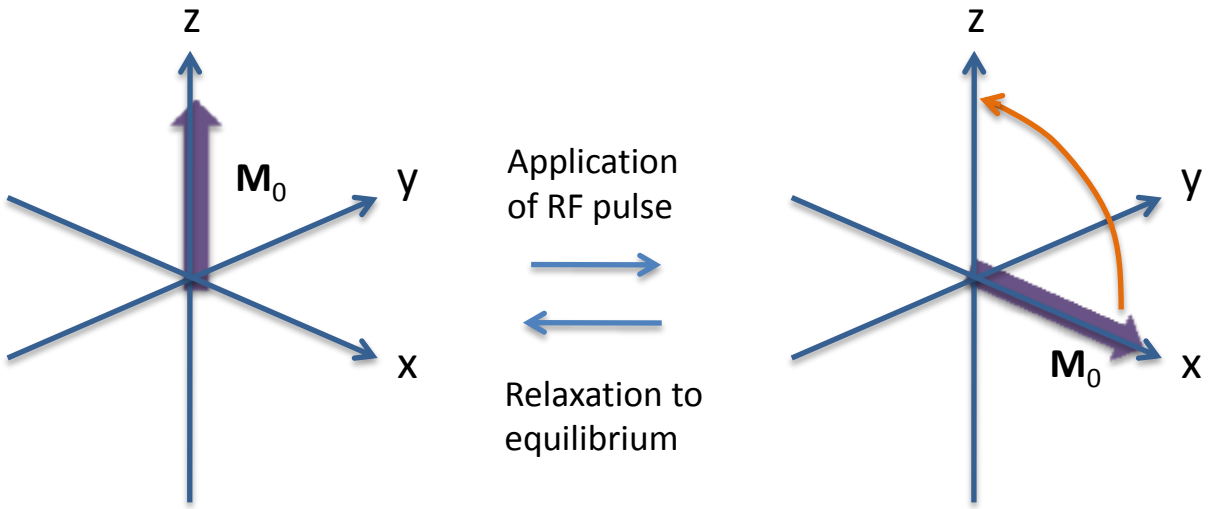
Relaxation: NMR relaxation processes

- T_1, spin-lattice, longitudinal relaxation. Magnetisation offset vector returning to align with the external magnetic field, the z-axis. Frequency of motions in megahertz (MHz).
- T_2, spin-spin, transverse relaxation. Magnetisation offset vector loses phase coherency in the xy plane. Process occurs alongside T_1 relaxation. Frequency of motions in hundreds of hertz.
- $T_{1\rho}$, relaxation under RF, relaxation in the rotating frame. Similar to T_2 relaxation, except relaxation is under spin lock. Frequency of motions in kilohertz (kHz).
- $T_{1\rho}$ relaxation is strictly not a NMR relaxation process, but an experiment. However, in rigid materials it becomes useful.

Spin-lattice relaxation

- T_1 (spin-lattice) relaxation. Magnetisation offset vector realigning with direction of magnetic field, the z axis.

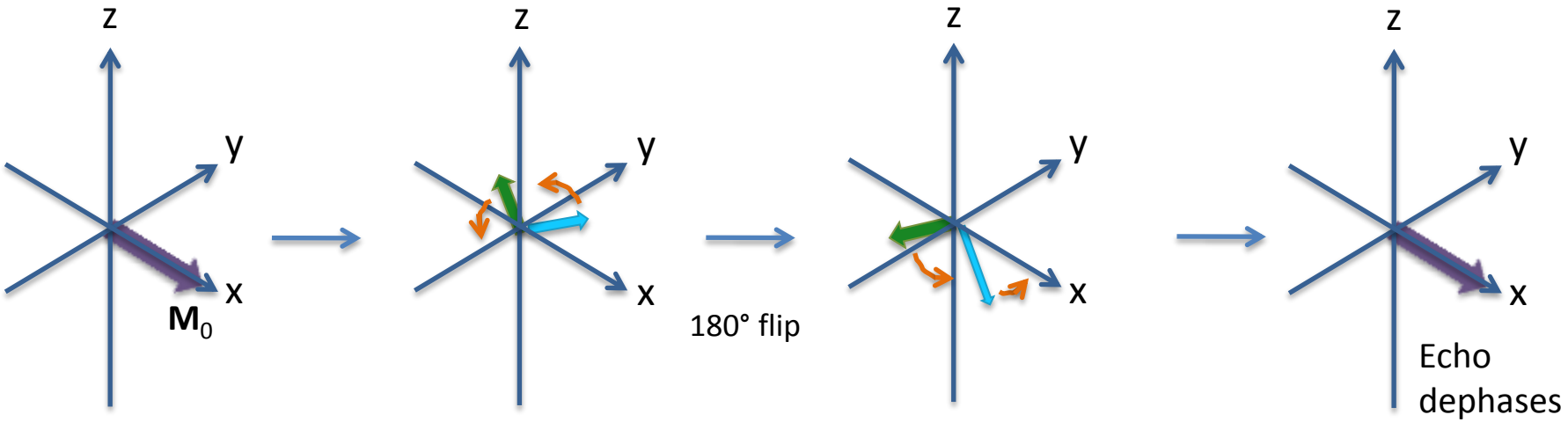
- 'Lattice' refers to surrounding system. Energy from pulse dissipated into lattice, dependent on molecular motion and dipolar interaction.



Spin-spin relaxation

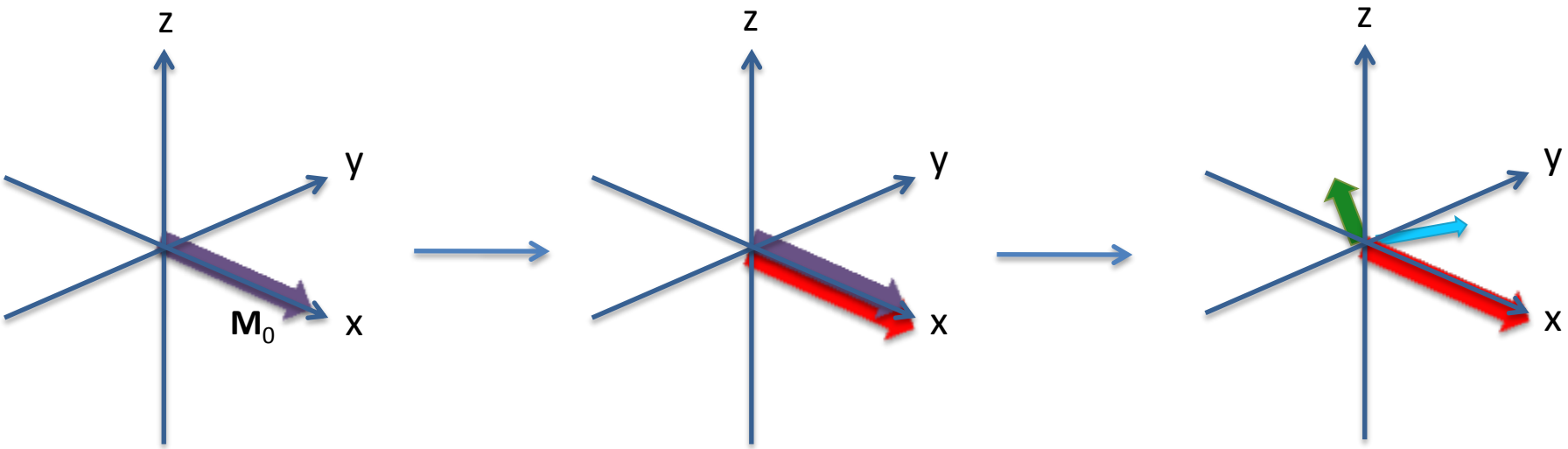
- T_2 relaxation is lose of phase coherency in the xy plane. Identification of distinct regions (crystalline and amorphous); these regions are polarised by the RF pulse with different efficiency, thus when they relax, separation occurs.

- Relaxation of separate regions happens at the same time, but at different speeds.



Relaxation under RF

- $T_{1\rho}$, relaxation under RF, uses a RF pulse to 'spin-lock' magnetisation. The magnetisation then dephases in a similar manner to transverse relaxation, loss of phase coherency in the xy plane.



RF (spin lock) pulse applied

Components relaxing separately

Relaxation; Summary

- Relaxation times vary as molecular motion increases/decreases.
- T_1 relaxation fastest when frequency of molecular motion equals resonance frequency.
- T_2 relaxation increases as molecular motion increases.

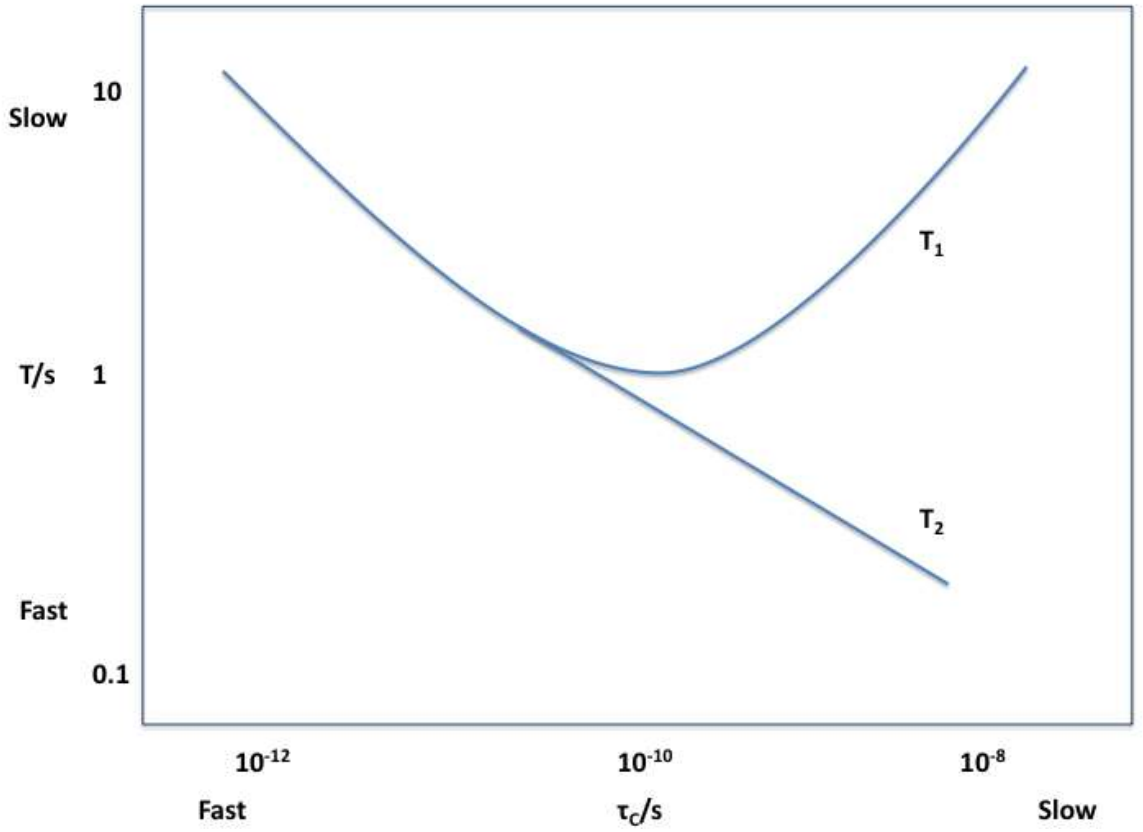
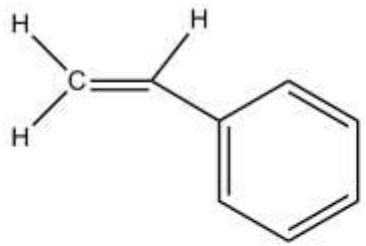


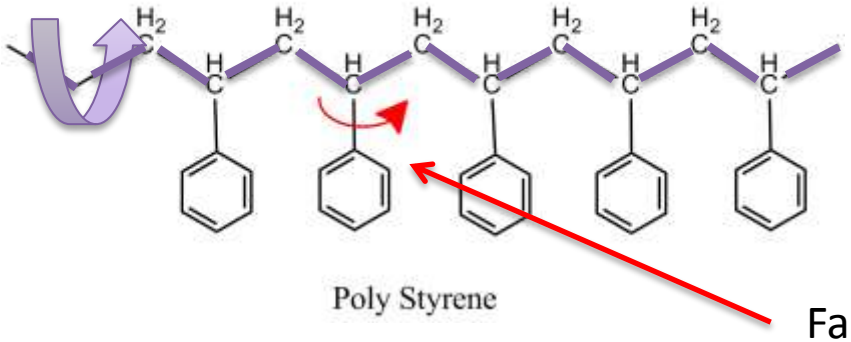
Figure 4. Difference in T_1 and T_2 relaxation with molecular motion

Motions in polymers

- Non-destructive technique.
- Use in combination with other characterisation techniques enhance understanding of material.



STYRENE



Poly Styrene

Slow rotations- kHz and 100's of Hz frequency. $T_{1\rho}/T_2$ relaxation.

Fast rotations- MHz frequency. T_1 relaxation.

Figure 5. Rotations in a styrene polymer.

Motions in polymers

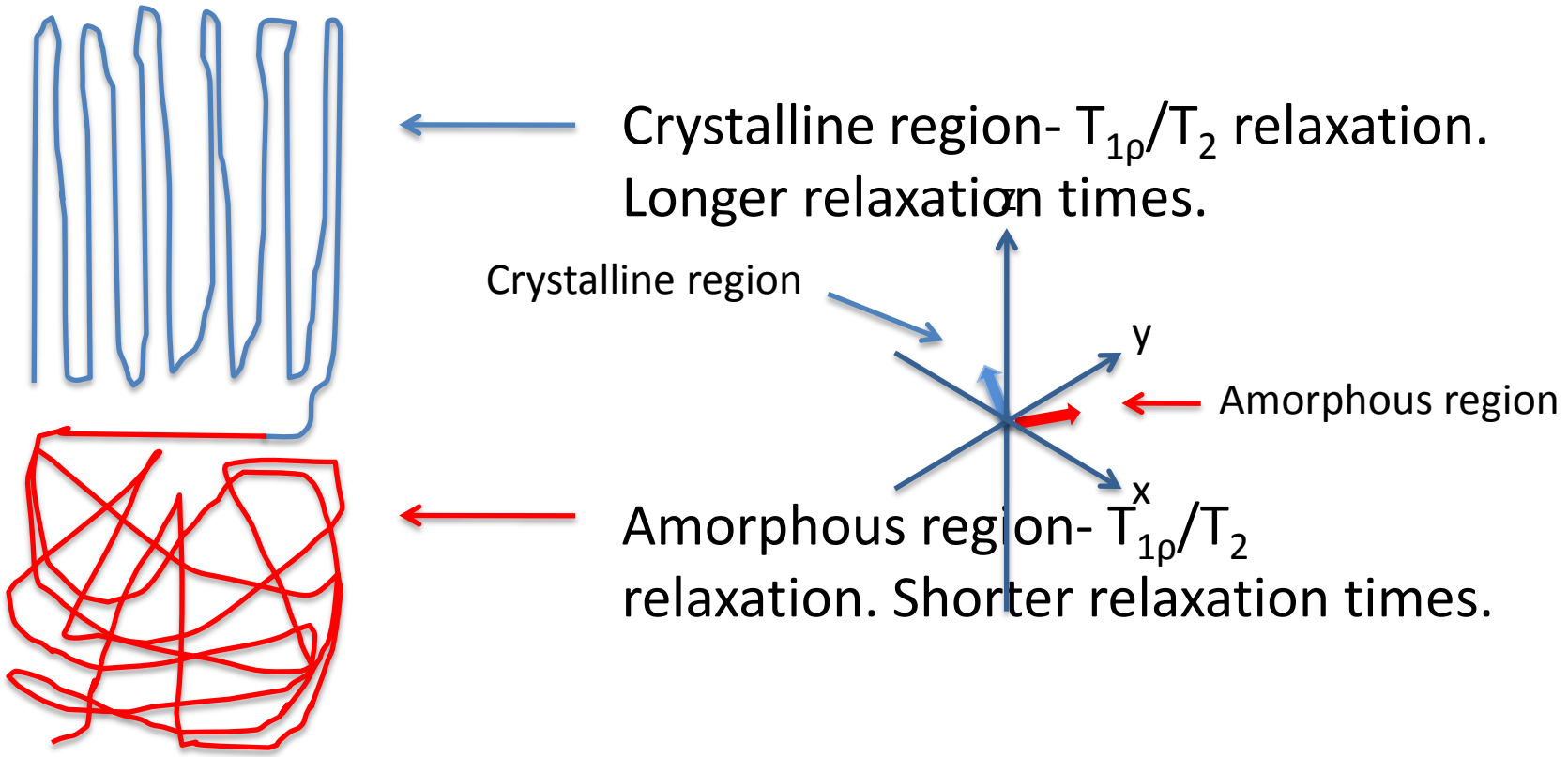


Figure 6. Cartoon representation of part of a semi-crystalline polymer.

What about totally amorphous materials?

Motions in polymers

- Crystalline/amorphous vs order/disorder?
  - Regions of increased order in an amorphous polymer?
  - Can this be observed by TD-NMR? Is there a difference between crystalline/amorphous and order/disorder relaxation?
- Thermal transitions?
  - Can anything be learnt from TD-NMR that, for example, Differential Scanning Caliometry (DSC) does not show?
- Can we observe differences in polymers from the same monomer system, but of different molar ratio?

Example; Polyvinyldiene fluoride (PVDF)

- PVDF is a well characterised semi-crystalline polymer (40% crystalline).
- T_1 relaxation dependent on molecular motion as a function of temperature.
- Relaxation profile similar to theory.

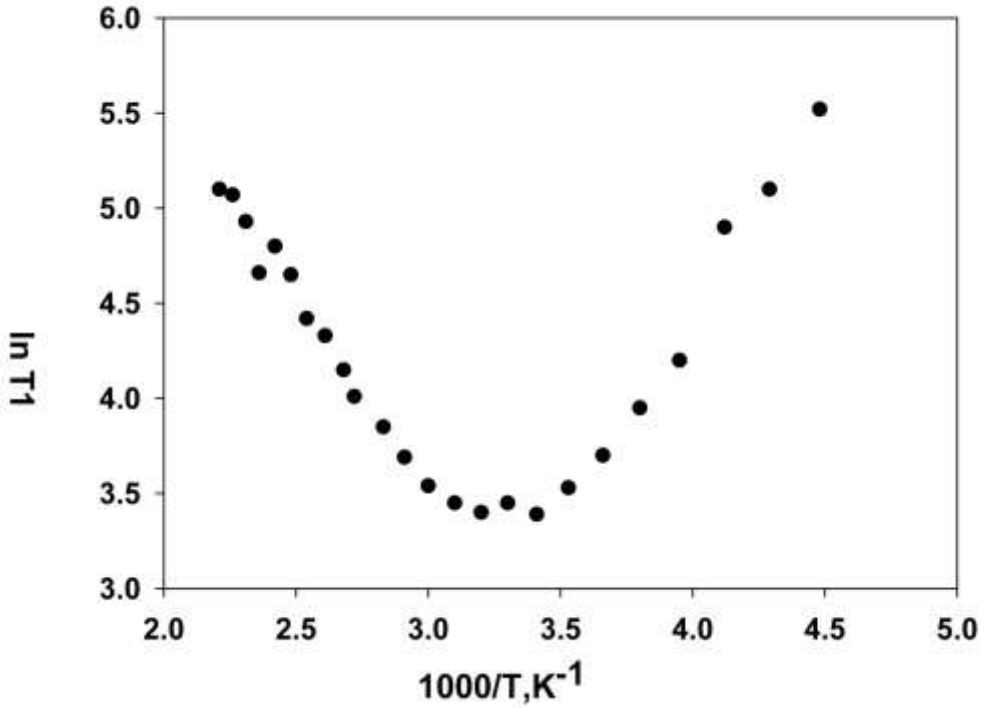


Figure 7. T_1 relaxation profile of PVDF from -50°C to +180°C

Example PVDF

- PVDF shows two distinct regions; attributed to amorphous and crystalline regions.
- Two dips in trends due to the glass transition (T_g) and pre-melt phase transitions (amorphous and crystalline respectively).
- Changes in motion pin-pointed to particular phase.

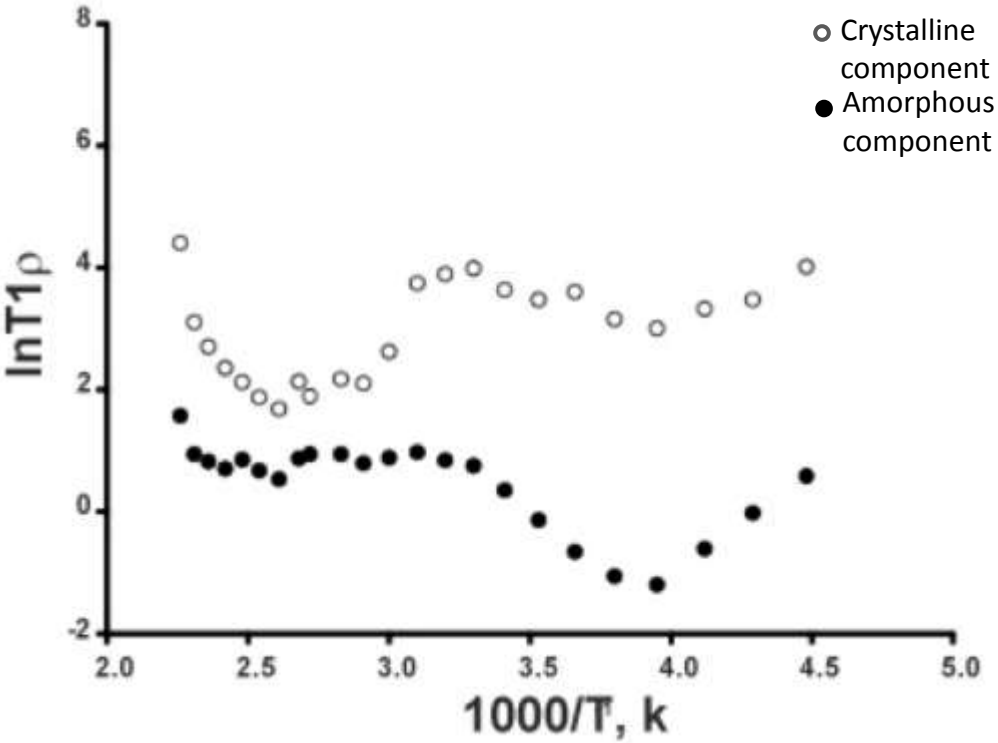


Figure 8. $T_{1\rho}$ relaxation profile of PVDF from -50°C to +180°C

Low density polymer materials

- RAFT S-*co*-MMA polyHIPEs: T_1 and T_2 times change as method of synthesis changes. RAFT polyHIPEs vs free-radical polymerised (FRP) polyHIPEs.

Table 1. T_1 and T_2 relaxation times for PS-*co*-MMA low density foams.

Synthesis method	T_1 (ms)	$T_{1\rho}$ (ms)		T_2 (ms)
RAFT	320±9	0.7 ± 0.2	6.6 ± 0.2	$8.3 \times 10^{-3} \pm 8 \times 10^{-5}$
FRP	449±3	0.7 ± 0.2	6.3 ± 0.3	$9.9 \times 10^{-3} \pm 2 \times 10^{-5}$

- S-*co*-DVB polyHIPEs: different T_1 time with different molar ratio.

Table 2. T_1 relaxation times for PS-*co*-DVB low density foams.

Polymer recipe S:DVB	T_1 (ms)
2:1	385±10
1:2	277±9

Summary

- Relaxation processes are dependent on molecular motion (temperature and molecular weight).
- Each relaxation process probes different molecular motion due to different frequency of motion seen by each relaxation process.
- Together, the relaxation processes can tell us more about the behavior of the material.

- TD-NMR has shown that ordered/disordered regions, in the highly characterised PVDF. Phase transitions seen by $T_{1\rho}$.
- S-*co*-DVB polyHIPE show differences in fast motion by T_1 relaxation.
- S-*co*-MMA polyHIPE differences in T_1, and T_2 relaxation time based on synthetic method attributed to molecular structure and weight.

Future work

- Analysis of $T_{1\rho}$ and T_2 relaxation times for varied molar ratio S-*co*-DVB polyHIPEs.
    - Can we see thermal transitions? If so, does this change as a function of the change in molar ratio? Comparison to other characterisation techniques?

- Continued analysis of S-*co*-MMA polyHIPEs synthesised by RAFT and FRP.
    - $T_{1\rho}$ analysis; does this differ from T_2 relaxation?

- Aerogel analysis; comparison of materials of the same composition synthesised by different methods.

Acknowledgements

- To the AWE Outreach fund.
- To Dr Wigen Nazarov for the continued support and ideas.
- To Dr Nick Bazin, Dr Simon Pitts, Mrs Lyn Kent and Mr Doug Faith for support, ideas and providing characterisation.
- To Dr Philip Wormald (St Andrews) for producing the T_1 and $T_{1\rho}$ graphs for PVDF.

- Thank you for listening!

Characterisation Challenges Facing Aerogel and Foam Manufacture for Laser Plasma Physics Experiments

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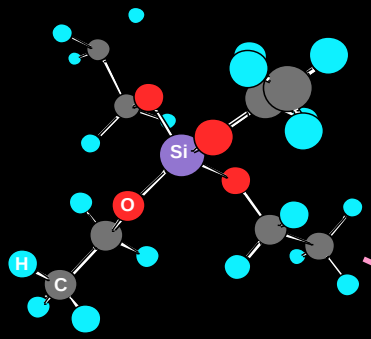
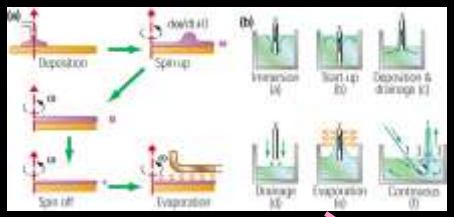
Introduction

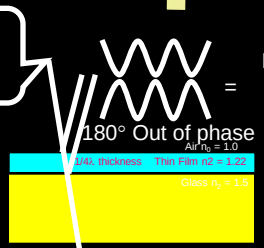
- General introduction to Solgel and Aerogels
  - Control of gelation
  - CO_2 exchange route
  - Direct solvent extraction
- Characterisation
  - Composition
  - Pore size
  - Density
    - Moisture analysis
- Summary and Conclusions

Over view of Sol-Gel processing



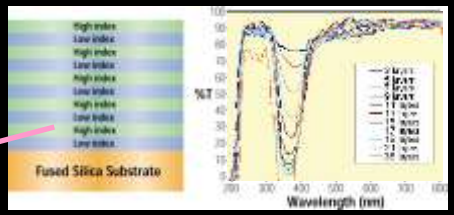


Light at normal incidence



= No reflection

100% Transmission



TEOS water catalyst solvent

Hydrolysis? Condensation

Coating

Xerogel film

Heat

Dense film

Wet gel

Gelation

Drying

Xerogel

Heat

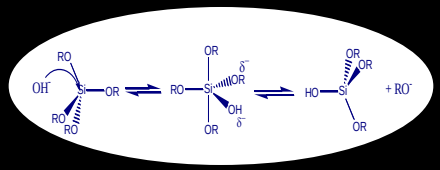
Dense ceramic

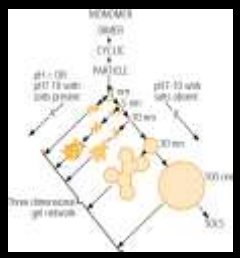
Super critical drying

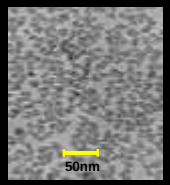
Aerogel

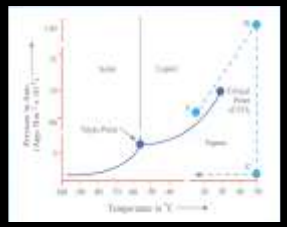
Uniform particles

Precipitation







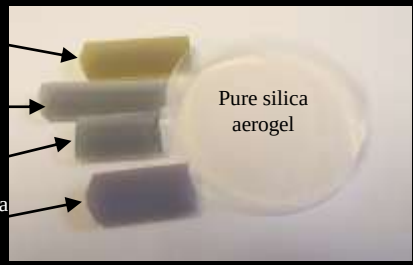


Cu loaded silica aerogel

Ta loaded silica aerogel

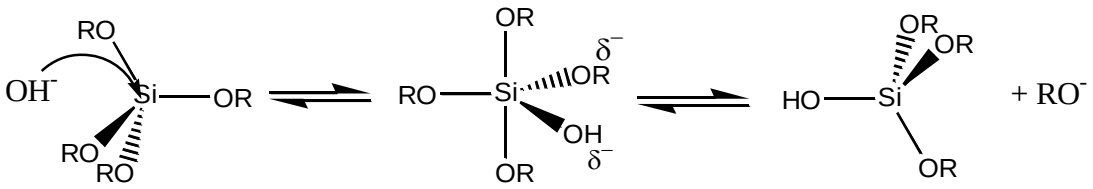
Pt loaded silica aerogel

Au loaded silica aerogel

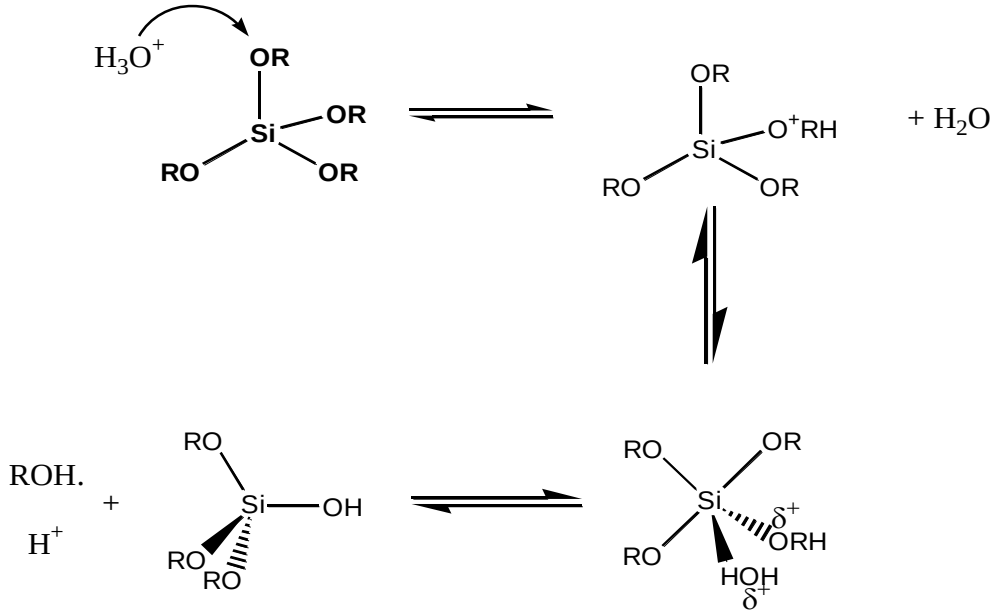


Control of gelation

- Base catalysed
  - Colloidal particles sticking together

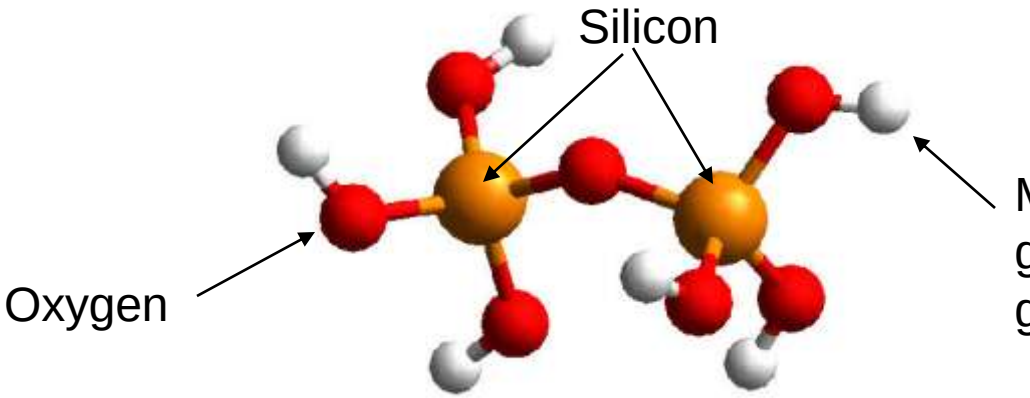


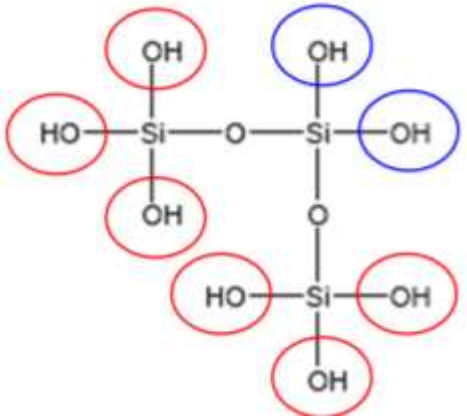
- Acid catalysed
  - Interconnecting polymeric strands.



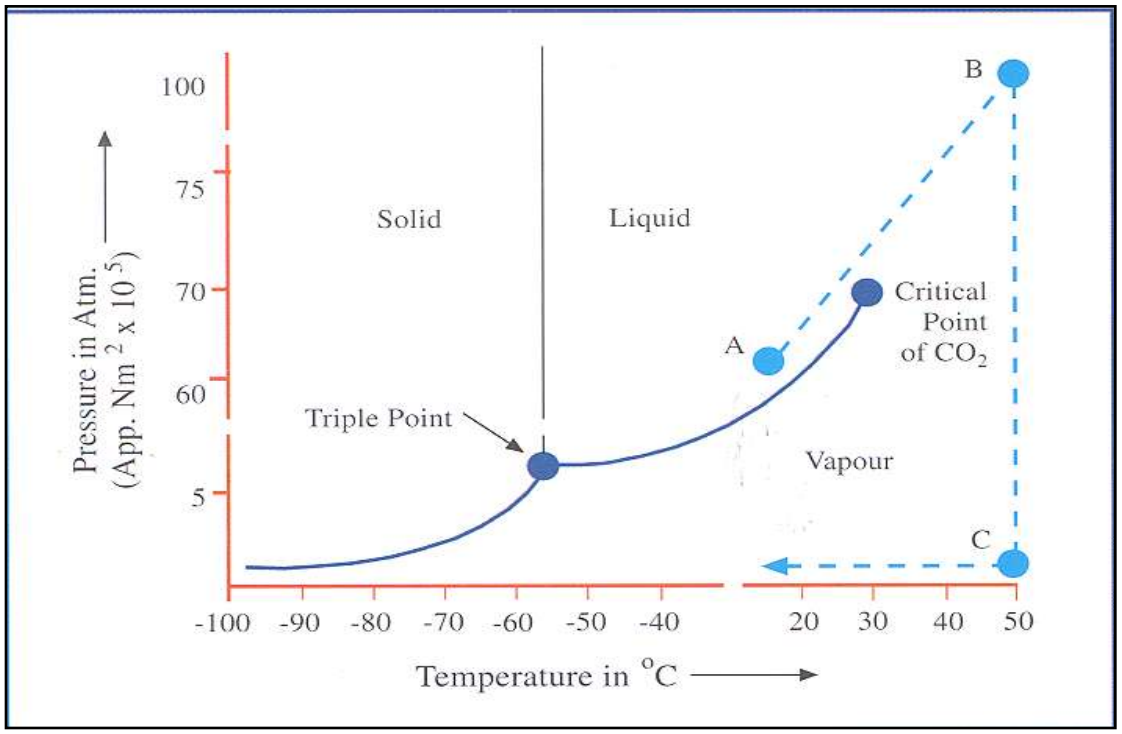
Monomer, dimers and trimers and polymers

- When two monomers react together they form a dimer and all six ligands are equivalent.
- Note, with a trimer there are now 2 ligand groups which are not equally exposed.

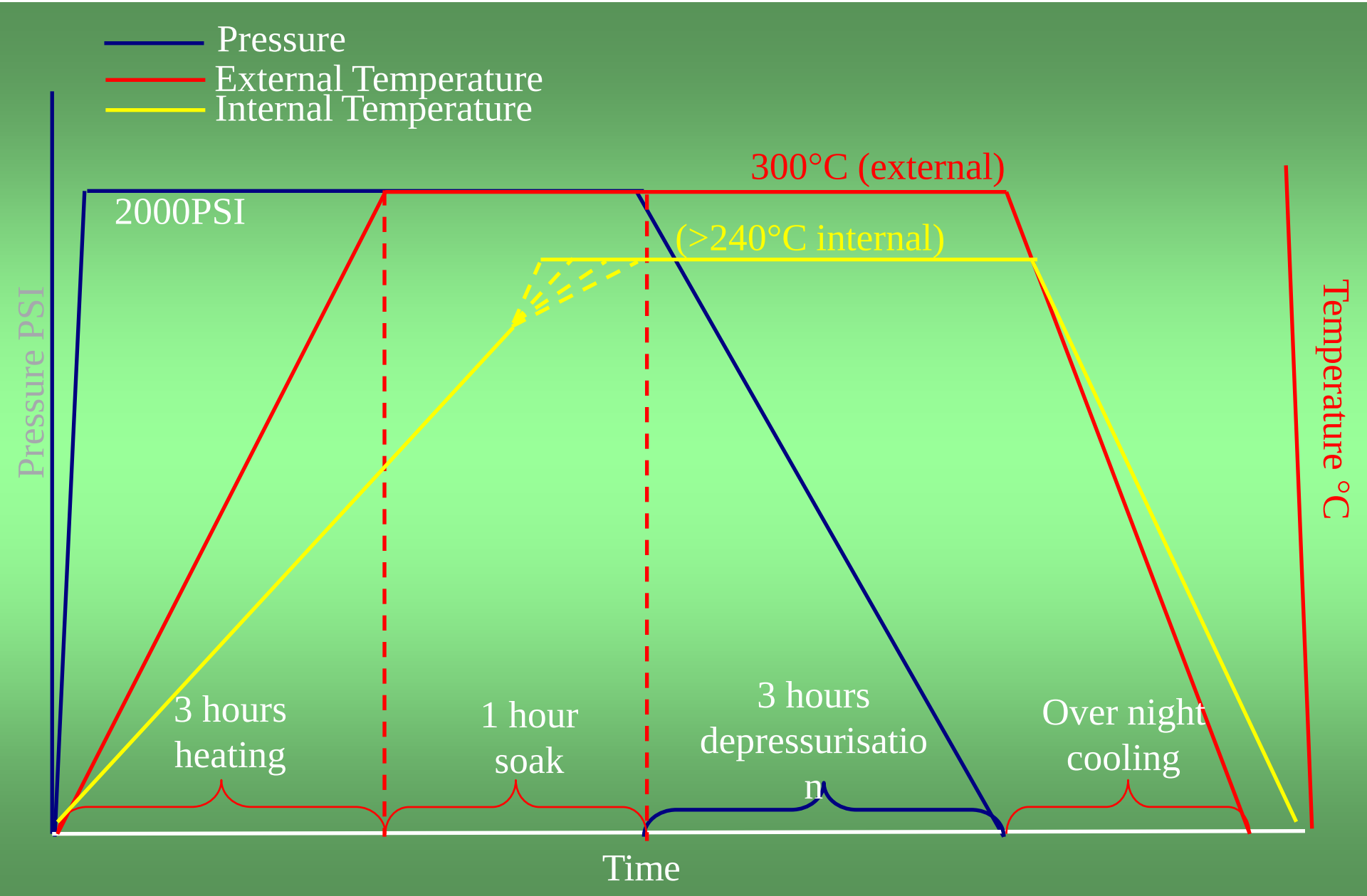




Phase diagram and pressure chamber for for CO_2 extraction



CPD Process


Pressure
External Temperature
Internal Temperature
300°C (external)
2000PSI
(>240°C internal)
Pressure PSI
Temperature °C
3 hours heating
1 hour soak
3 hours depressurisation
Over night cooling
Time

Characterisation (foams in general)

- Composition (carbon content)
- Pore size
- Density
  - Moisture

Elemental analysis

TEST REPORT

WAS: 19385 **Sample ID**: Silica aerogel **Sample Type**: Solid

Technique	Element	Units	Result	Date
SOP 31	Carbon	%wt/wt	5.42	16-Jun-11
	Hydrogen		1.15	
	Nitrogen		0.00	

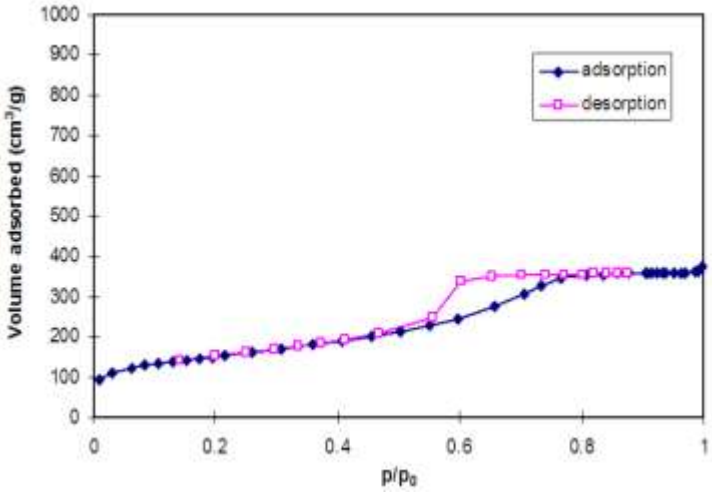
Semi-Quantitative Scan ▼ SOP 64

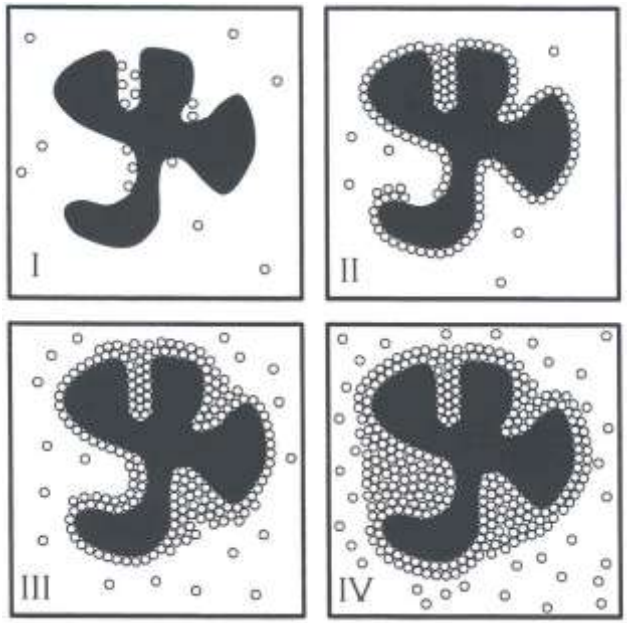
ICP:Al	ppm wt/wt	140	<10	ICP: Rb	ppm wt/wt	20	30	23-Jun-11
As		<20	<20	Rh		<20	<20	
Bi		60	60	Sb		<20	<20	
Ca		20	<10	Se		<100	<100	
Ce		<20	<20	Sn		<30	<30	
Fe		30	20	Te		<50	<100	
Ge		20	20	Tl		50	50	
P		<30	<30	U		<30	<30	
Pb		30	30					

During the Semi-quantitative scan the sample was analysed for:-
Ag,Al,As,Au,Bi, Ba,Be,Ca,Cd,Ce,Co,Cr,Cu,Dy,Er,Eu,Fe,Ga,Gd,Ge,Hf,Hg,Ho,Ir,K,La,Li,Lu,Mg,Mn, Mo,Na, Nb,Nd,Ni,Os,P,Pb,Pd,Pr,Pt,Rb,Re,Rh,Ru,Sb,Sc,Se,Sm,Sn,Sr,Ta,Tb,Te,Th,Ti,Tl,Tm,U,V,W,Y,Yb,Zn,Zr.
Unless otherwise stated, all readings above 10 ppm have been reported although to get a true result they need individual analyses.

Pore size

- Not routinely measured for aerogels.
- Nitrogen adsorption (BET surface area analysis) is a standard technique for measuring high surface are materials and pore sizes and shapes.





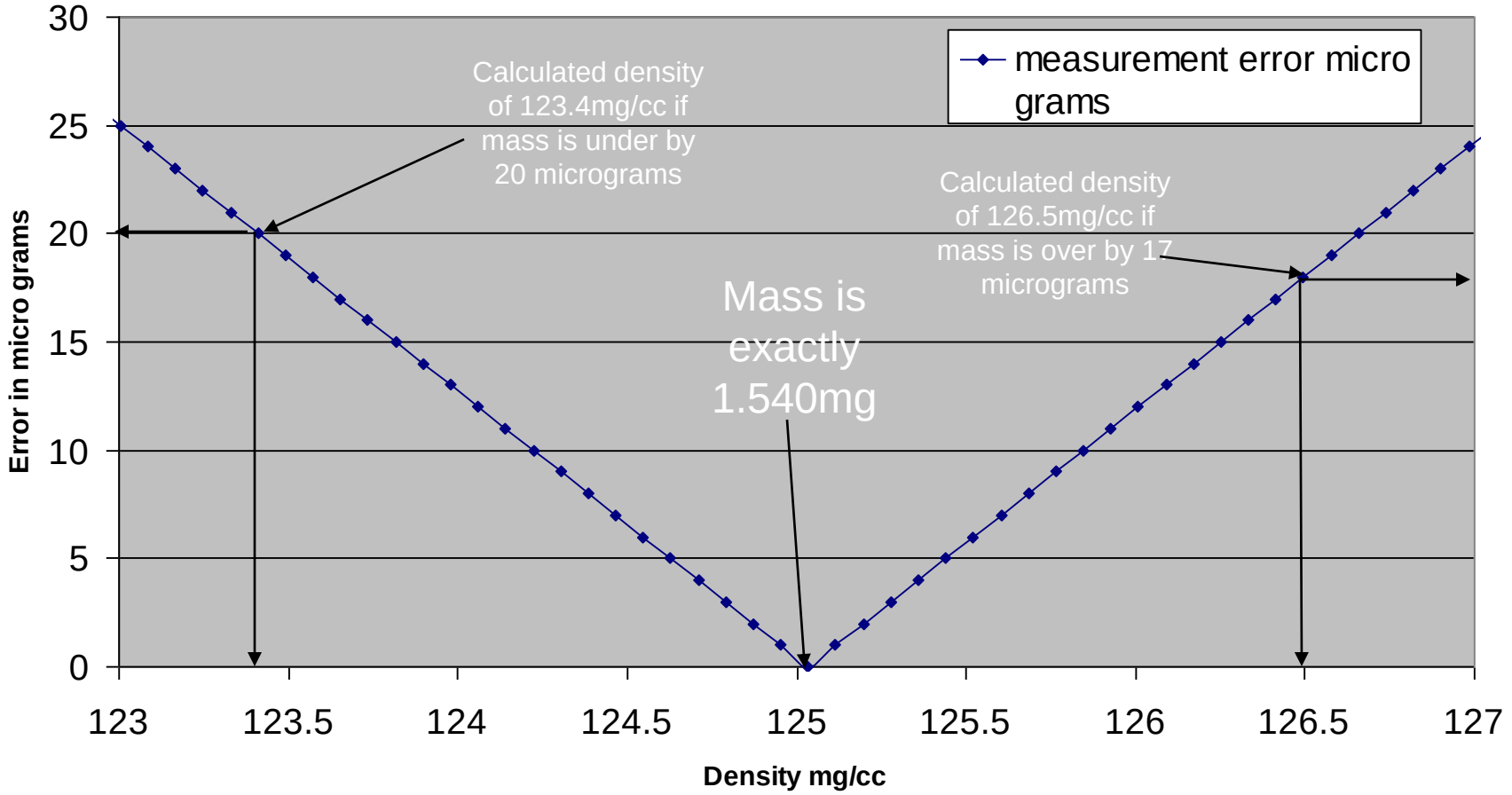
Density

- Has a few hidden features.
- The simplest method is to measure the mass and the dimensions, calculate the volume and hence density.
- Limitations
  - Errors in these measurement manifest in errors in the density
  - Cannot account for density gradients
  - Change in the parameters will change the density

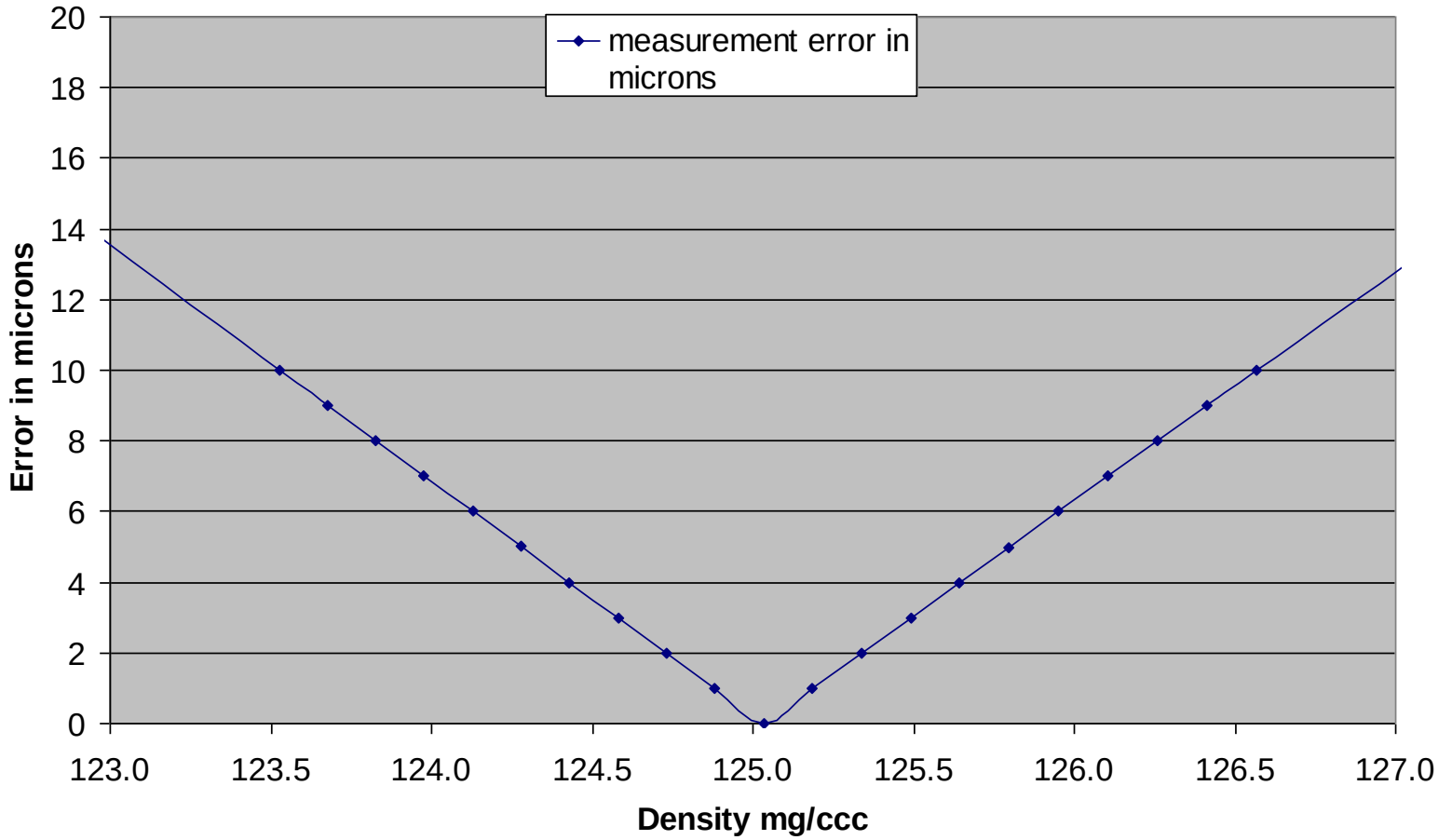
Measurement error

- For mass measurement the situation isn't too bad.
  - 1) Its a mechanical technique (low human error).
    - Possible static and sample damage
  - 2) Seven figure micro balances are routinely available (although expensive!)
- The volume isn't measured its calculated, the length and diameters are measured.
- Errors are a function of
  - Measurement accuracy
  - Operator error
  - Initial size
  - Surface /internal defects

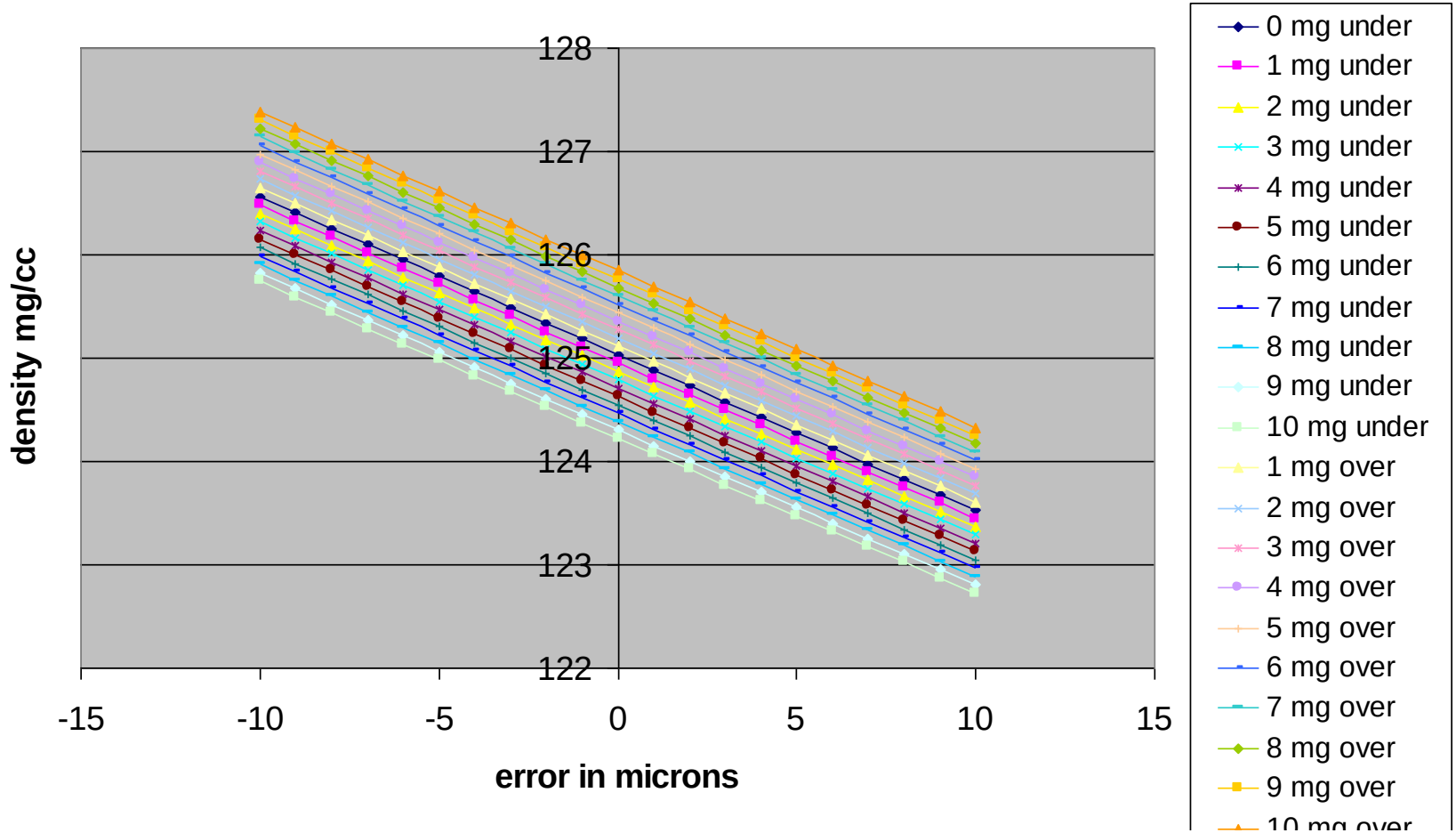
Density as a function of mass for a 2mm diameter by 2.8mm long foam cylinder



If you under measure by 9 microns your density goes up by 2 mg/cc and vice versa (assuming accurate mass)

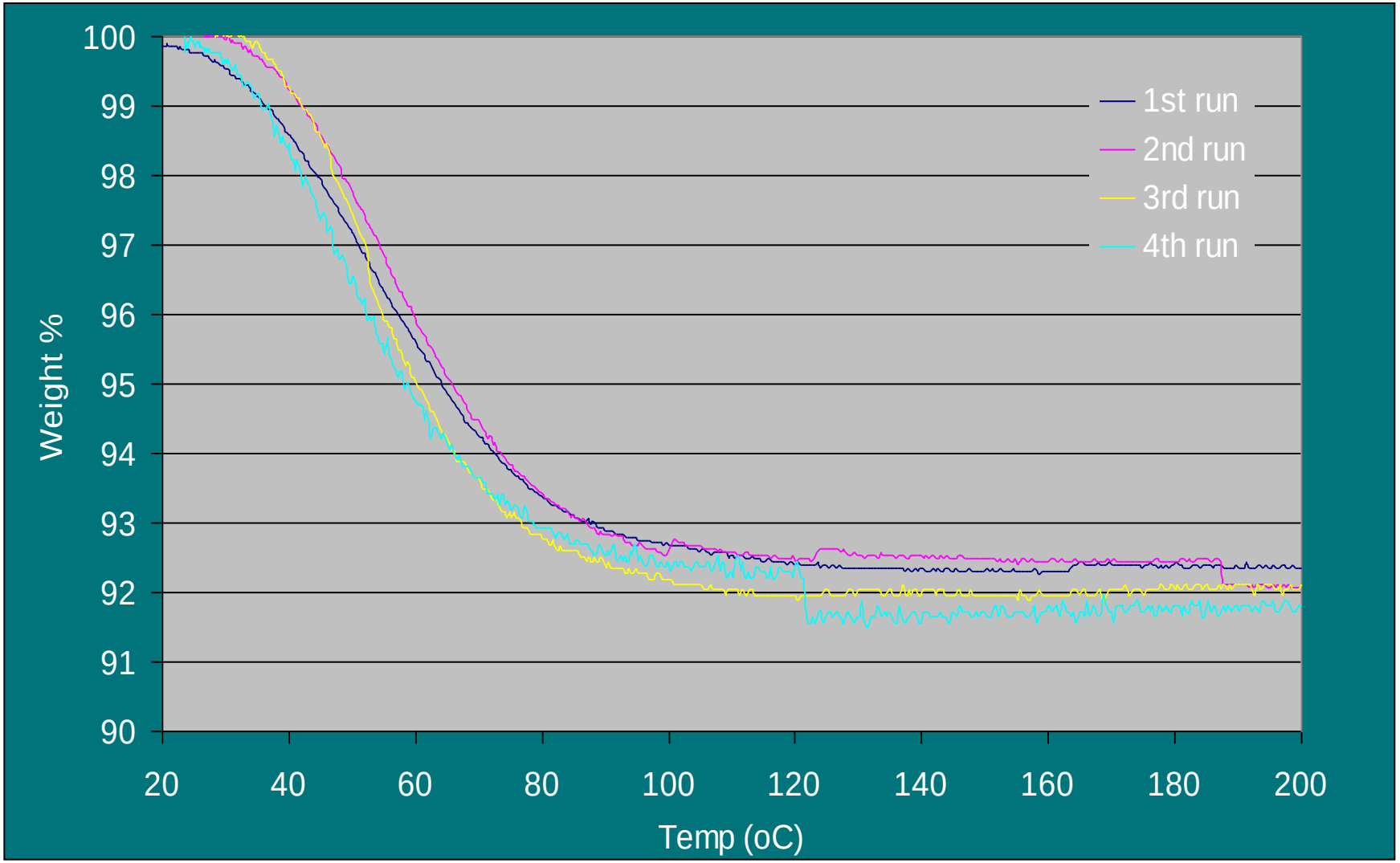


Putting it all together

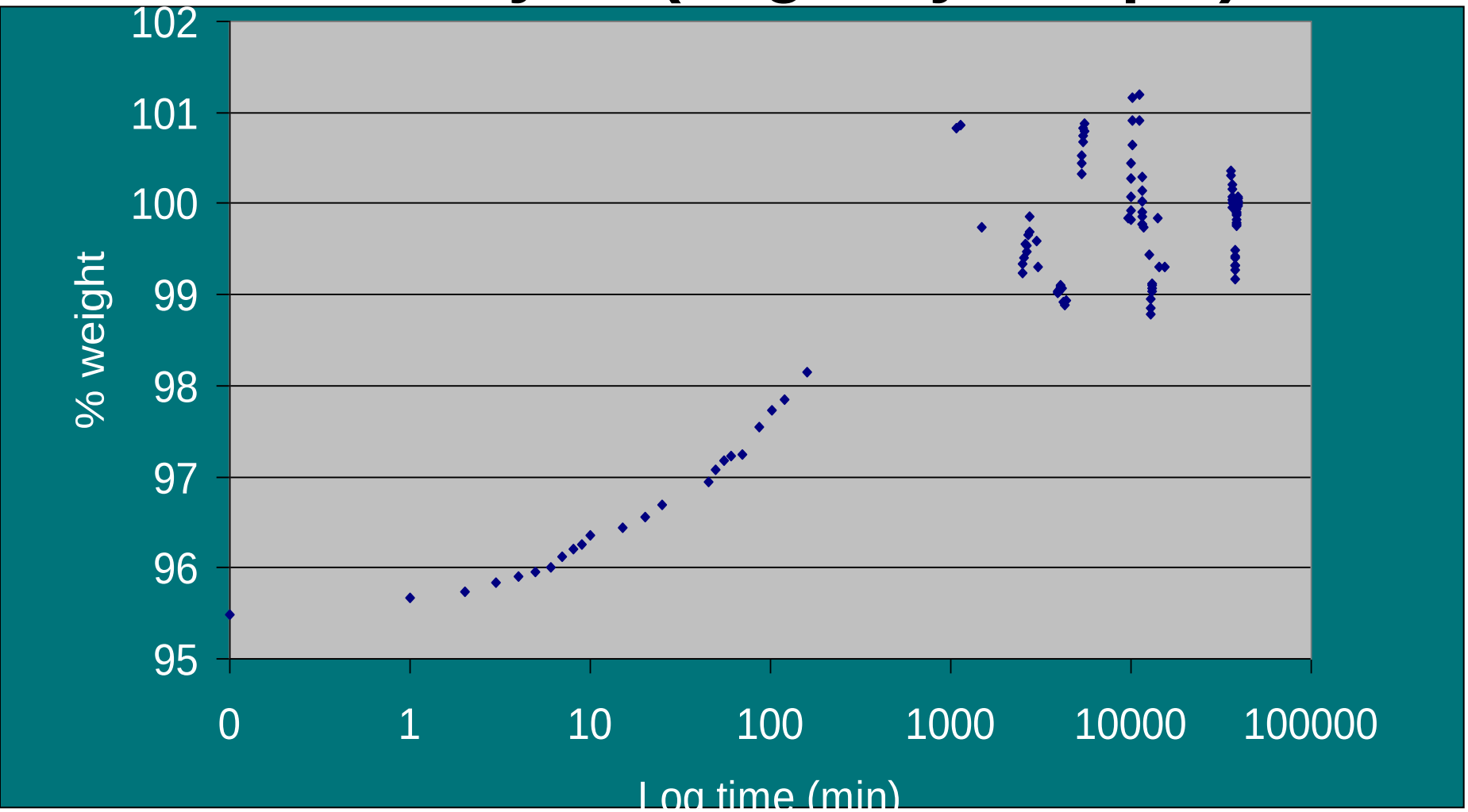


Moisture analysis

- The issue
  - Aerogels and foams in general are highly porous low density materials capable of holding large amounts of moisture.
  - This amount is dependent of the local environment and the surface nature of the material.
  - For silica derived through the CO_2 exchange route this can prove quite a challenge.

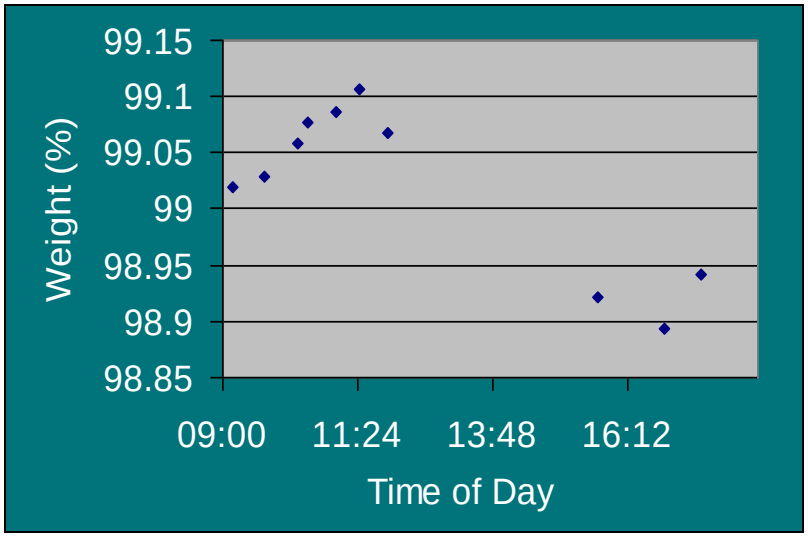

100
99
98
97
96
95
94
93
92
91
90
Weight %
20
40
60
80
100
120
140
160
180
200
Temp (oC)
1st run
2nd run
3rd run
4th run

Moisture analysis (large dry sample)

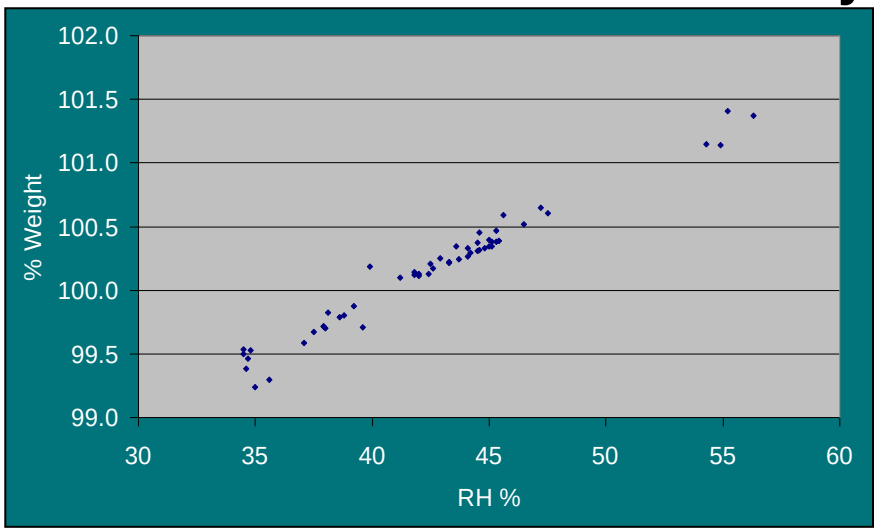


Moisture analysis (Daily fluctuation)

- 1g sample in the laboratory environment.
- Daily fluctuation



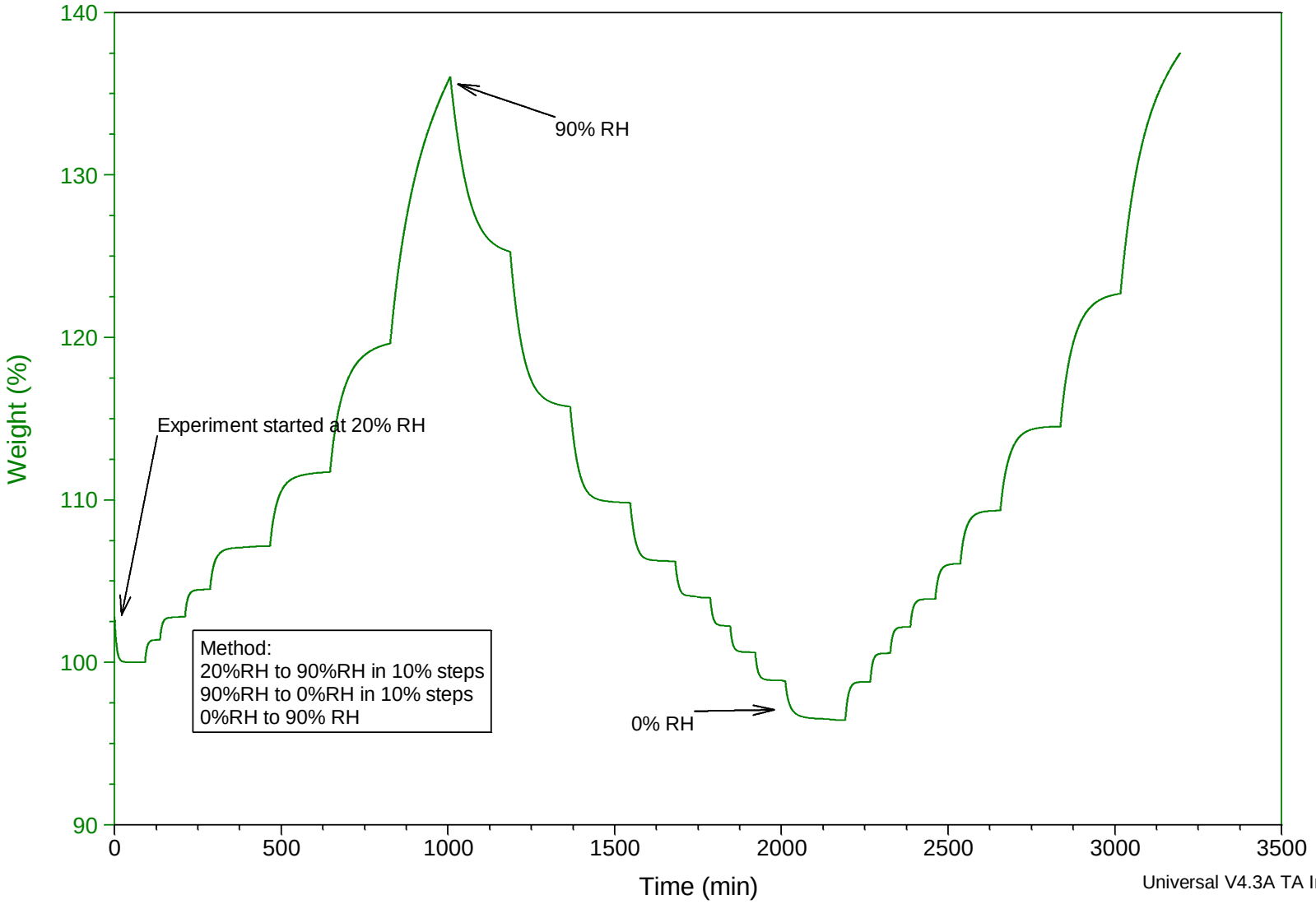
Correlation with relative humidity



Sample: Sample Received by TA Instrument
Size: 7.3335 mg
Method: Hydro Gel

TGA

File: D:...\PROJECTS\AWE\Bazin\Hydrogel1.001
Operator: Paul
Run Date: 05-Feb-2007 21:27
Instrument: TGA Q5000 V3.1 Build 246



Universal V4.3A TA Instruments

Vacuum assessment of moisture

- Targets will be placed in a chamber, evacuated for a period of time and then the laser is fired.
- Issues of interest.
  - How much moisture is on the target
    - a) before entering the chamber,
    - b) during evacuation and
    - c) how much remains after evacuation.

Other methods of determining Density

- Xray transmission/absorption (See Talk tomorrow)
- Displacement (for volume)
  - Good for irregular objects.

Summary, conclusion, acknowledgments and questions.

- You only make what you measure. If you can't measure it you haven't made it.
- Foams present many challenges due to both their chemical and physical composition.
- Many thanks to the materials team at AWE:
  - Tina Jewell, Cheryl Macqueen, Paul Simmonds and Doug Faith*.
- More foams and characterisation tomorrow at 11am.

POSTERS COME AND SEE US (Sav, Steve, Marc, Maria, Colin & Wigen) FOR A FEW BEERS & A CONVIVIAL CHAT!