Australian Government

ANSTO

Capabilities and Advances in High-Resolution Surface Characterisation Technique at Australian Synchrotron Infrared Microspectroscopy (IRM) Beamline

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ANSTO – Australian Synchrotron

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Science. Ingenuity. Sustainability.

OVERVIEW

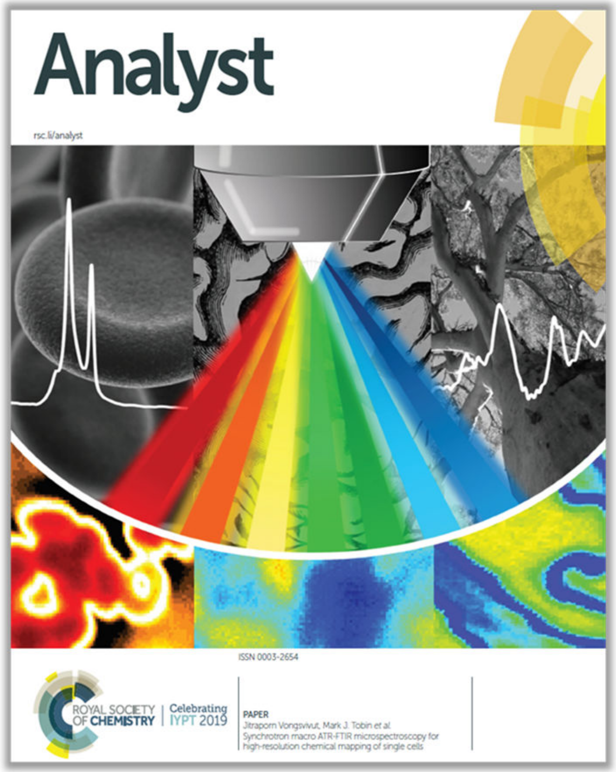
1 In-House Developed Macro ATR-FTIR Technique

MODEL 1: "Hybrid" macro-ATR

- Food Science – Dairy Research

MODEL 2: "Soft-contact" piezo-controlled macro-ATR

- Materials and Interfacial Science
- Electrochemistry in Battery Research



2 Macro ATR-FTIR Applications in other disciplinary

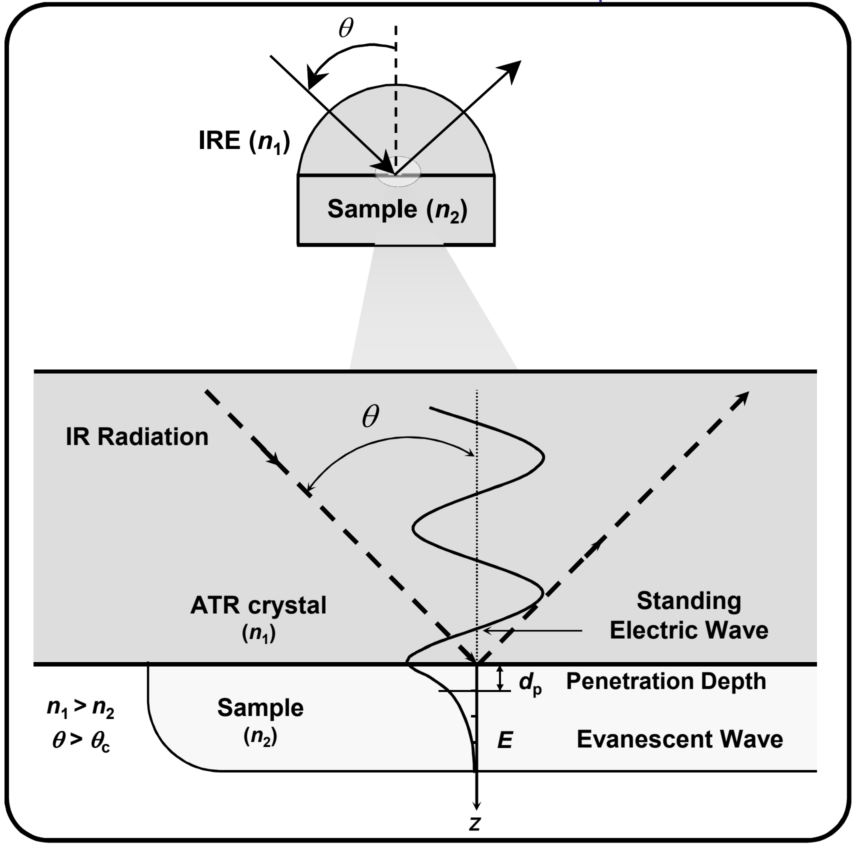
- Biomedical Science
- Single Fibres
- Composite Materials
- Forensic science → Rhiannon Boseley (1 PM)
- Archaeology → Justyna Miszkiewicz (1.30 PM)

Ref: J. Vongsvivut, D. Perez-Guaita, B.R. Wood, P. Heraud, K. Khambatta, D. Hartnell, M. Hackett, M.J. Tobin, "Synchrotron macro ATR-FTIR microspectroscopy for high-resolution chemical mapping of single cells," *Analyst* (2019) **144**, 3226-3238.

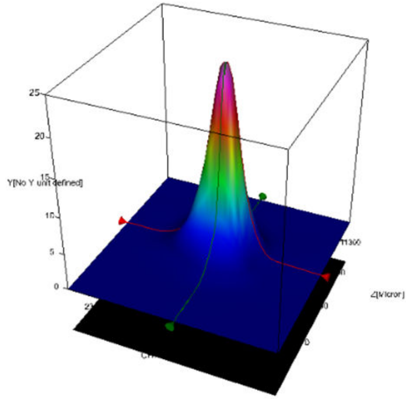
In-House Developed Macro ATR-FTIR Technique

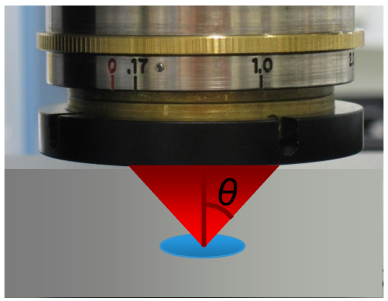
PRINCIPLE OF ATR-FTIR SPECTROSCOPY

ATR-FTIR utilizes **TOTAL INTERNAL REFLECTION** phenomenon when IR radiation travels through high index ATR crystal and impinges on low-index sample surface at $\theta_{incident} > \theta_c$ resulting in evanescent wave, which decays exponentially into sample surface (d_p).



spatial resolution with total internal reflection





Rayleigh Equation:

$r = 1.22\,\lambda\ /\ 2 \times \boxed{NA}$

Numerical aperture

$NA = n(\sin\theta)$

At λ = 6 µm
For *NA* (air) = 0.65
***r* = 5.6 µm**

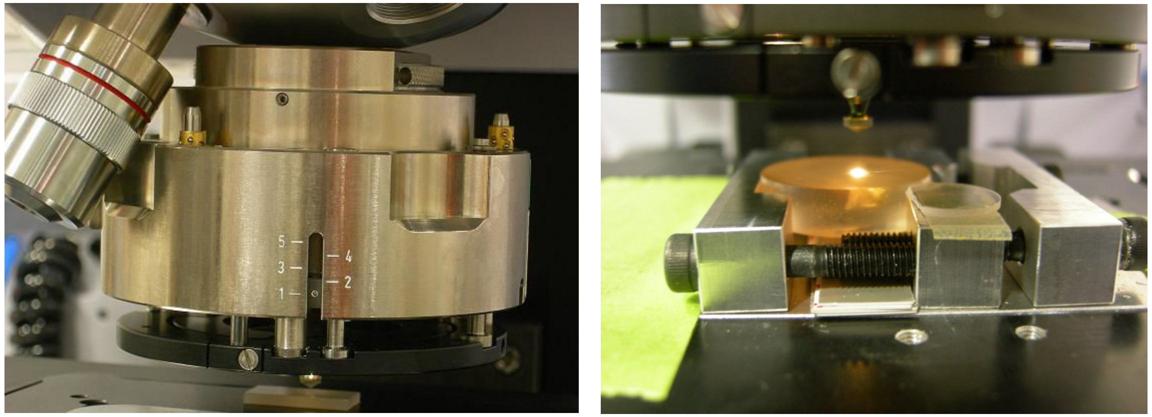
At λ = 6 µm
For *NA* (ZnSe) = 1.56
***r* = 2.3 µm**

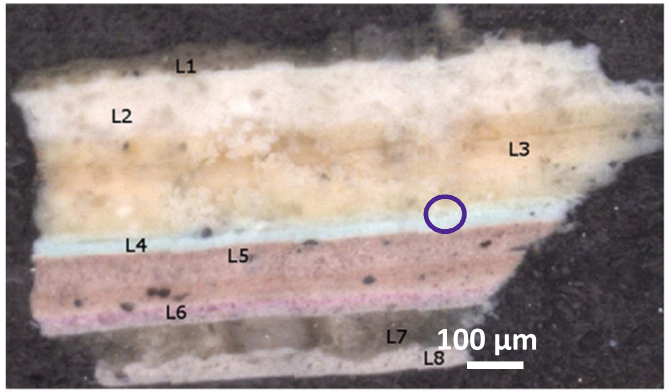
At λ = 6 µm
For *NA* (Ge) = 2.6
***r* = 1.4 µm**

Ref: J. Vongsvivut *et al.* Rapid determination of protein contents in microencapsulated fish oil supplements by ATR-FTIR spectroscopy and partial least square regression (PLSR) analysis, *Food Bioprocess Technol.* (2013) **7**, 265-277.

TRADITIONAL MICRO-ATR TECHNIQUE

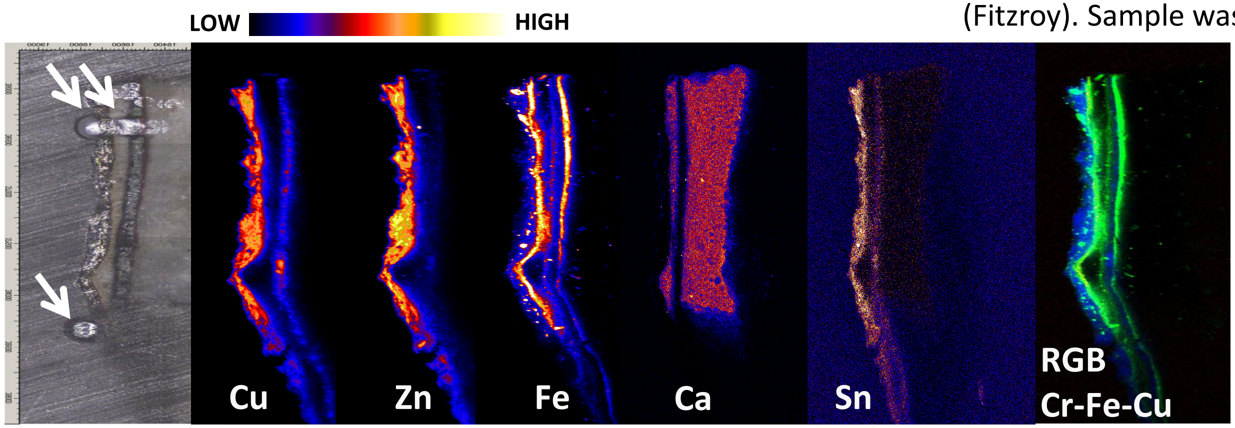
Bruker ATR 20× objective equipped with Ge-ATR crystal





Multilayer paint fragment from exterior of Provincial Hotel (Fitzroy). Sample was not suitable for thin sectioning.

- × **Sample damage**
- × **Contamination**
- × **Slow scan**



Visible image of a paint cross section recorded after standard micro-ATR "mapping" measurements (*left*), showing indentation marks damaged by the high pressure from the ATR crystal (*arrowed*)

Ref: R. Sloggett *et al.* Microanalysis of artworks: IR microspectroscopy of paint cross-sections, *Vib. Spectrosc.* (2010) **53**, 77-82.

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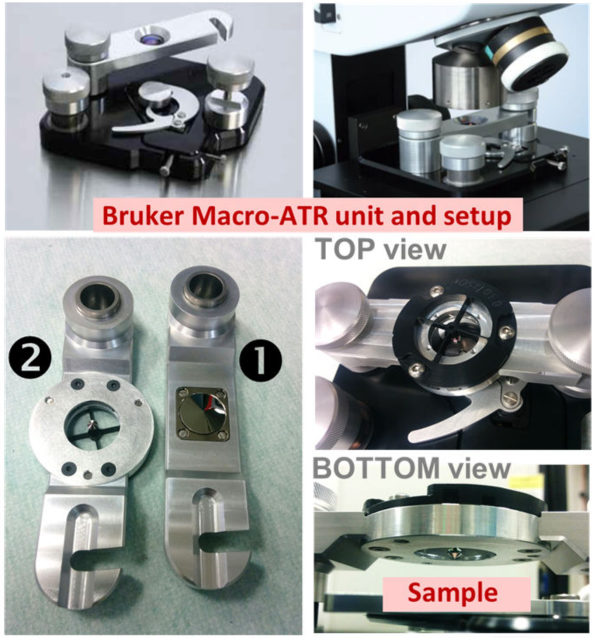
MODEL 1: “HYBRID” MACRO-ATR WITH 20× OBJECTIVE

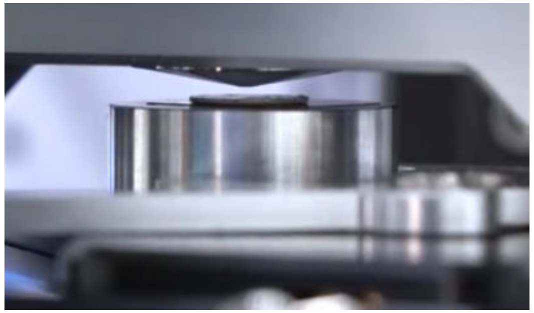


MACRO-ATR cantilever arm:

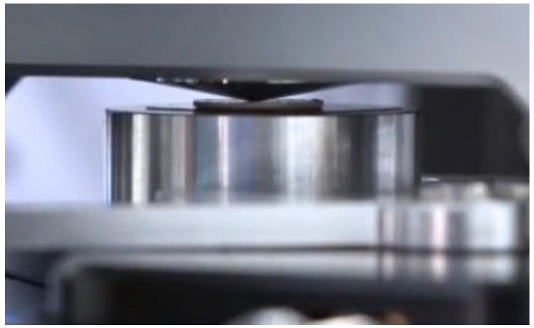
❶ **ORIGINAL model** supplied with 1-mm-dia facet Ge crystal.

❷ **HYBRID version:** in-house modification to accept 250-µm-dia and 100-µm-dia facet Ge crystals from commercial micro-ATR objectives.

Non-contact position for background measurement



Contact position for mapping measurement



- ✓ No cross contamination
- ✓ Minimal sample damage
- ✓ Faster scan

Available sizes of Ge facet tip: 1 mm, 250 µm and 100 µm

Ref: V.K. Truong *et al.* Evolution of silica nanoparticle-polyester coatings on surfaces exposed to sunlight, *J. Vis. Exp.* (2016) **116**, e54309.

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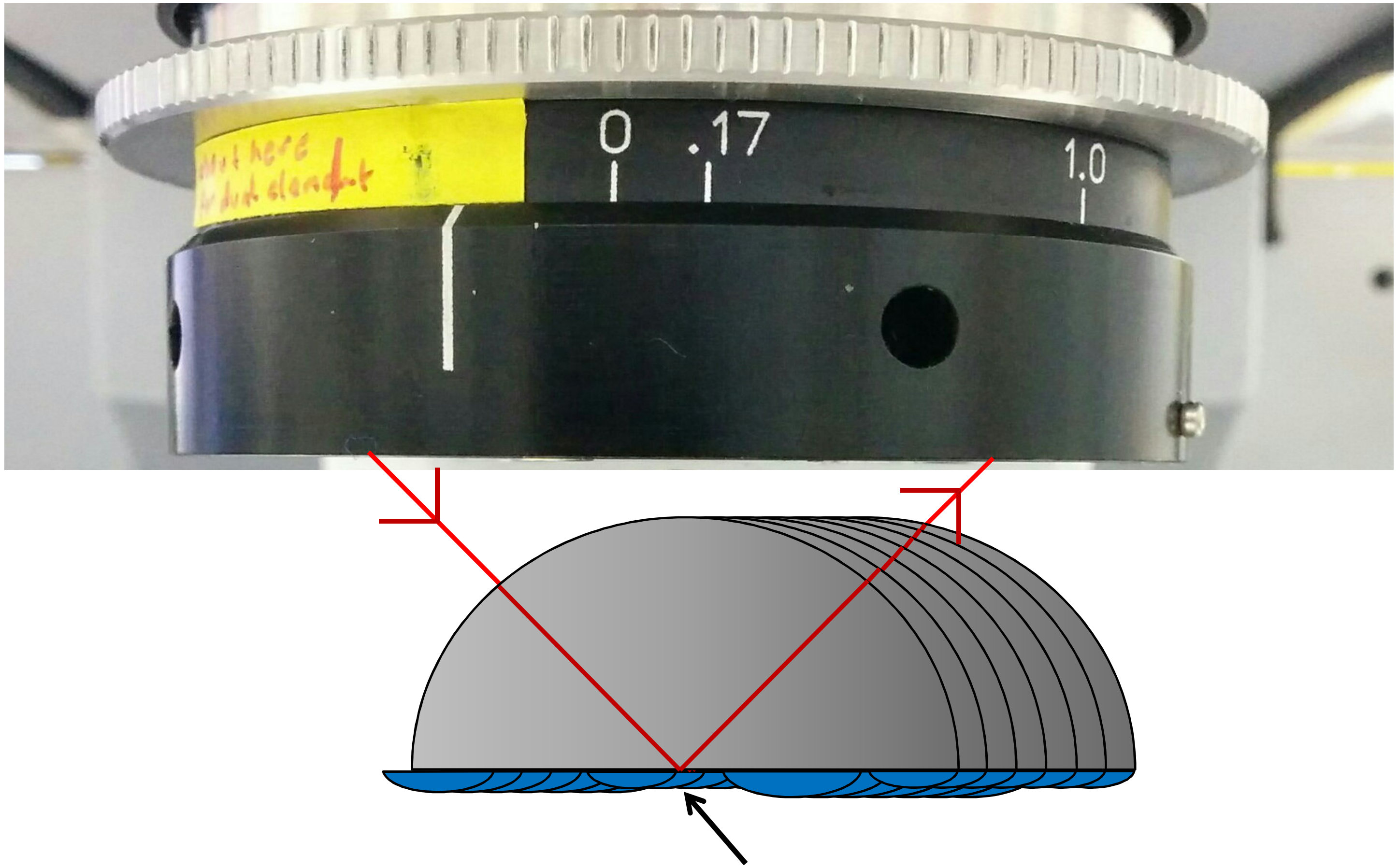
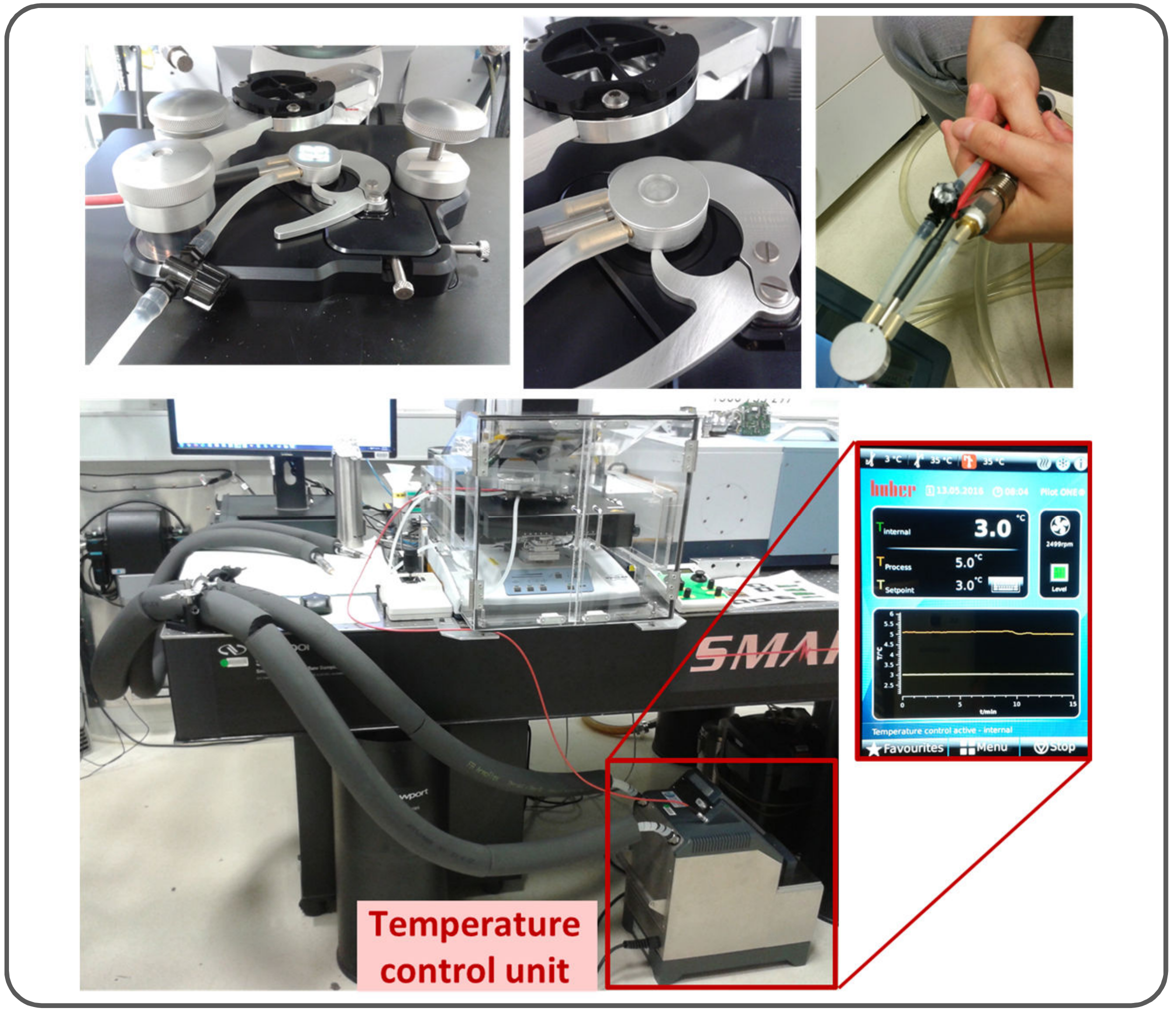
MODEL 1: "HYBRID" MACRO-ATR WITH 20× OBJECTIVE



Motion of point of beam focus is equal to stage step size / ATR refractive index

smallest focused beam size available = 1.8 μm | smallest step (lateral) resolution = 250 nm

Model 1: "Hybrid" Macro-ATR with 20× Objective



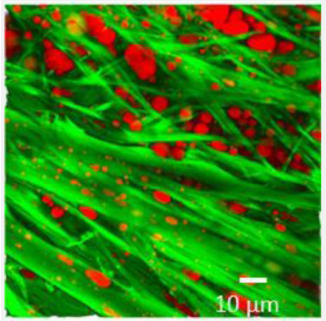
Ref: A.P. Pax *et al.* Characterisation of Mozzarella cheese microstructure using high resolution synchrotron transmission and ATR-FTIR microspectroscopy, *Food Chem.* (2019) **291**, 214-222.

MODEL 1: "HYBRID" MACRO-ATR WITH 20× OBJECTIVE

Understanding effect of processing condition on lipid and protein distribution in dairy products

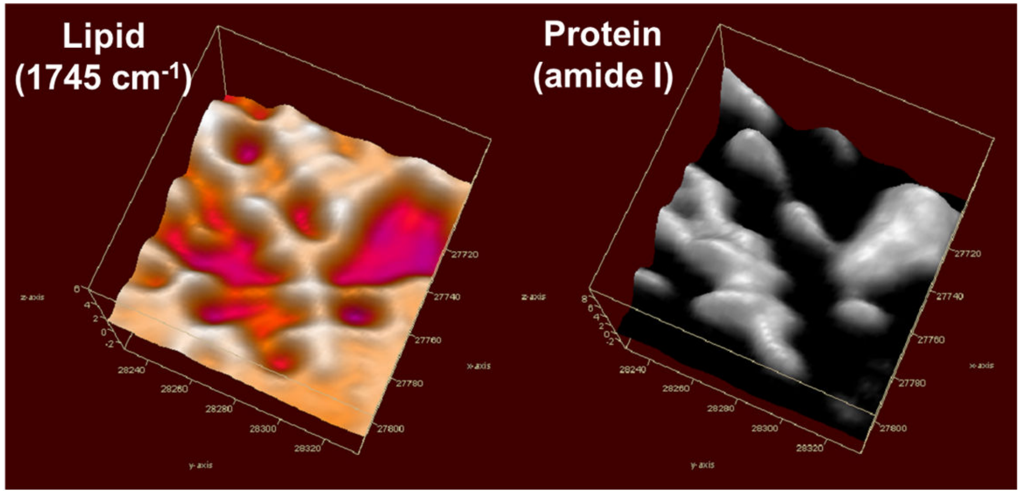
Australian Research Council Dairy Innovation Hub

Correlating chemical and physical properties with other indicators of product quality.



MACRO-ATR CHEMICAL MAPS OF GRUYÈRE CHEESE

(mapped area: 25×25 μm^2)



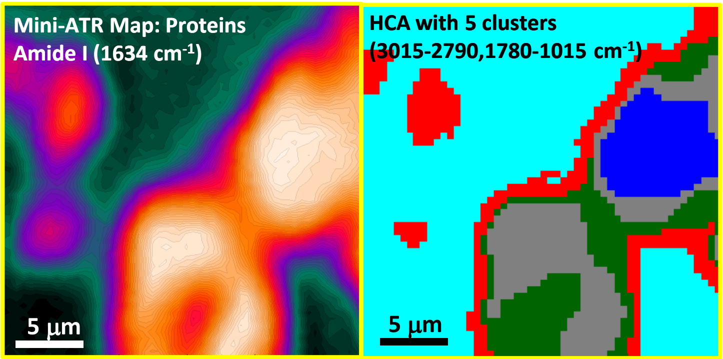
Combination of cool stage and HYBRID Macro-ATR allows acquisition of high-resolution lipid/
from fresh dairy product at a controlled temperature (e.g. 4°C) WITHOUT any sample preparati
in highly accurate analyses of the chemical compositions for optimisation and enhancement of prc

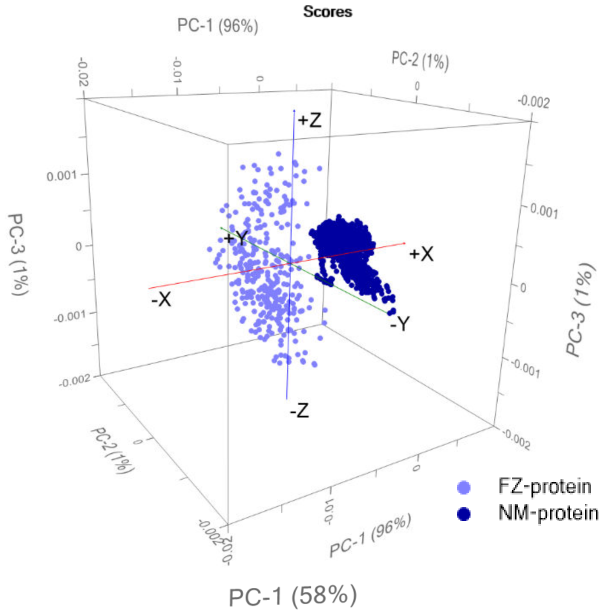
Ref: A.P. Pax *et al.* Characterisation of Mozzarella cheese microstructure using high resolution synchrotron transmission and ATR-FTIR microspectroscopy, *Food Chem.* (2019) **291**, 214-222.

MACRO ATR-FTIR: DAIRY RESEARCH

Control Mozzarella (stored at 4°C)

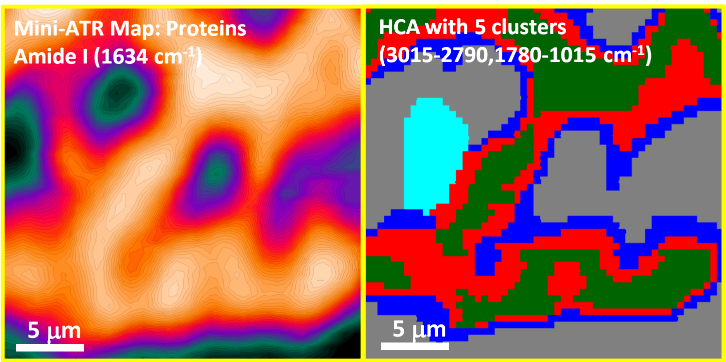
high resolution covering 27×27.5 μm² area

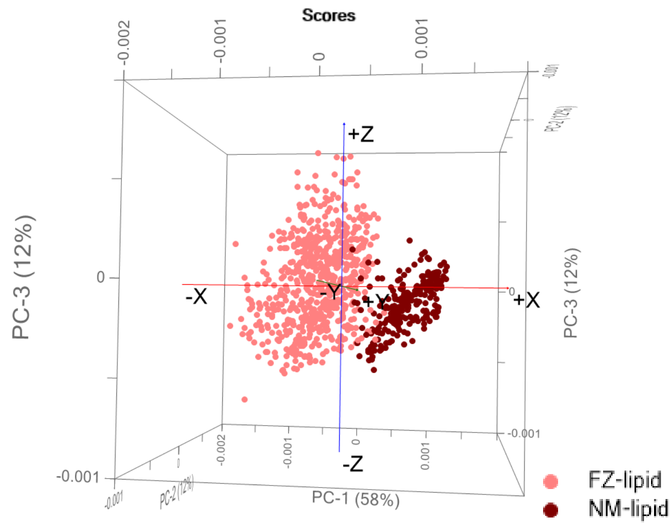




Frozen Mozzarella

high resolution covering 27×27.5 μm² area





Ref: A.P. Pax, L. Ong, J. Vongsvivut, M.J. Tobin, S.E. Kentish, S.L. Gras, "The characterisation of Mozzarella cheese microstructure using high resolution synchrotron transmission and ATR-FTIR microspectroscopic techniques," *Food Chem.* (2019) **291**, 214-222.

MODEL 2A: "SOFT-CONTACT" PIEZO-CONTROLLED MACRO-ATR

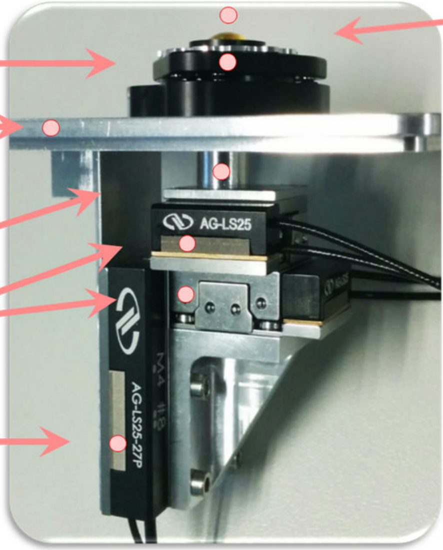
Magnetic mount

Microscope stage insert

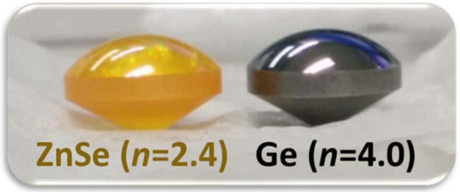
Sample support post

x-/*y*- sample translation stage

Closed-loop *z*-axis piezo linear stage

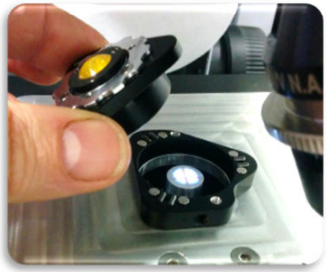


ATR hemispheres (radius of curvature = 7 mm)



ATR hemisphere in magnetic mount

1-mm-dia contact facet on underside (arrow)



Precise positioning achieved by using magnetic mount

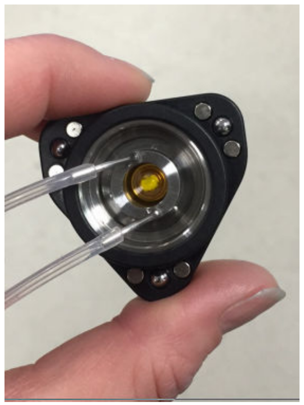
Using high numerical aperture (NA) objective to couple synchrotron-IR beam into the ATR hemisphere

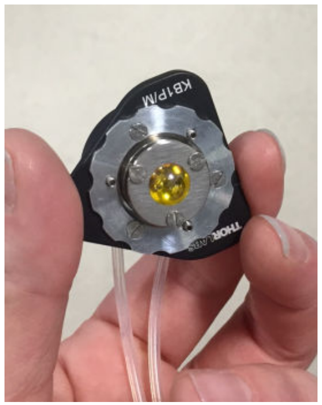
The device was developed for monitoring hydration & chemical build-up of polyelectrolyte multilayers (PEMs), and has been proved ideal for a wide range of very fragile materials.

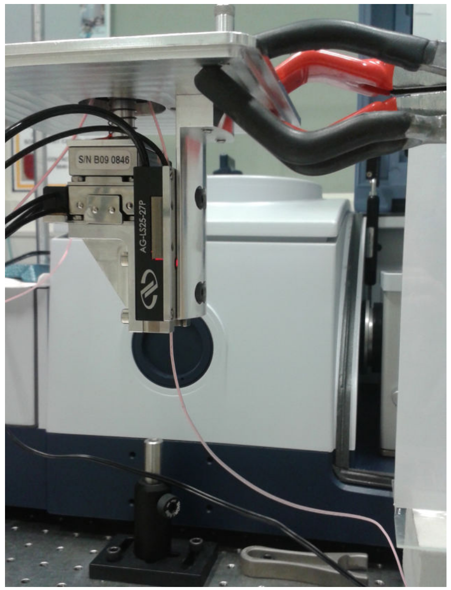
Ref: N.L. Benbow *et al.* A Novel Soft Contact Piezo-Controlled Liquid Cell for Probing Polymer Films under Confinement using Synchrotron FTIR Microspectroscopy, *Sci. Rep.* (2018) **8**, 17804.

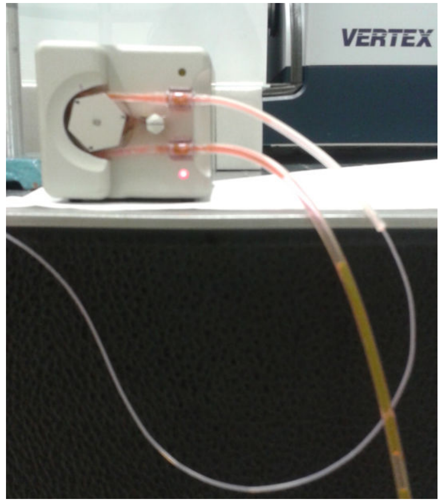
MODEL 2A: “SOFT-CONTACT” PIEZO-CONTROLLED MACRO-ATR

Adaptation into flow-cell ATR for *in-situ* hydration & chemical build-up of polyelectrolyte multilayers







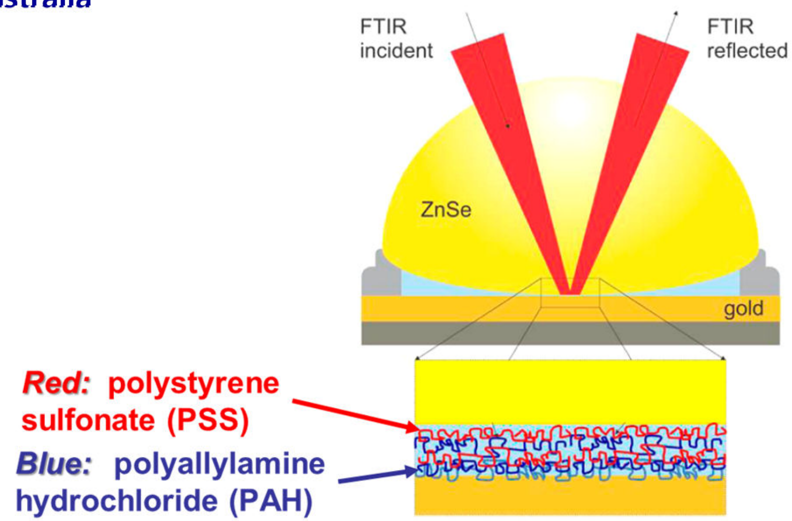


Ref: N.L. Benbow *et al.* Odd-even effects on hydration of natural polyelectrolyte multilayers: An in situ synchrotron FTIR microspectroscopy study, *J. Colloid Interface Sci.* (2019) **553**, 720-733.

MODEL 2A: "SOFT-CONTACT" PIEZO-CONTROLLED MACRO-ATR

University of South Australia

***In-Situ* monitoring of hydration and chemical build-up of polyelectrolyte multilayers (PEMs) using soft-contact piezo-controlled Macro ATR**



Optical diagram of soft-contact piezo-controlled Macro-ATR setup using a custom-made ZnSe hemisphere with curved underside as an ATR element, for studying hydration lubricant and shear-induced behaviours of confined PEMs.

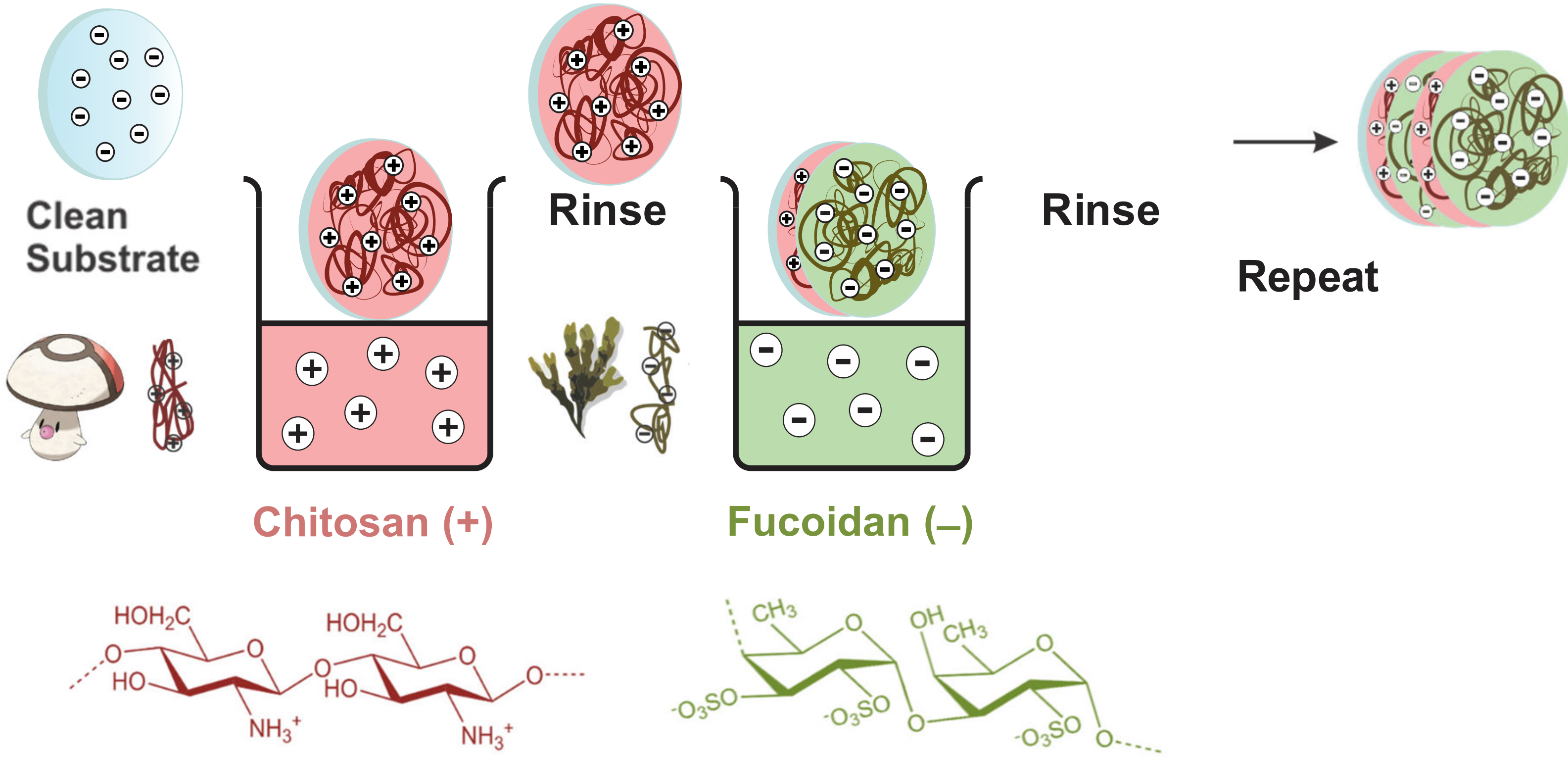
- Biopolymer gels have many applications including medical implant coating, contact lenses, drug delivery and scaffolds for tissue engineering.
- Hydration and behavior under "stress" of multilayers are important in overall performance.
- Experiment required study of hydrated multilayers under conditions of applied pressure.

Ref: N.L. Benbow *et al.* Odd-even effects on hydration of natural polyelectrolyte multilayers: An in situ synchrotron FTIR microspectroscopy study, *J. Colloid Interface Sci.* (2019) **553**, 720-733.

MACRO ATR-FTIR: MATERIALS & INTERFACIAL SCIENCE

University of South Australia

Polysaccharide Polyelectrolyte Multilayer (PEM) System



Ref [1]: D.A. Beattie, A. Beaussart, A. Mierczynska-Vasilev, S.L. Harmer, B. Thierry, L. Puskar, M. Tobin, *Langmuir* (2012) **28**, 1683-1688.
Ref [2]: T.M. Ho, K.E. Bremmell, M. Krasowska, S.V. MacWilliams, C. Richard, D.N. Stringer, D.A. Beattie, *Langmuir* (2015) **31**, 11249-59.
Ref [3]: N.L. Benbow, J.L. Webber, P. Pawliszak, D.A. Sebben, T.T.M. Ho, J. Vongsvivut, M.J. Tobin, M. Krasowska, D.A. Beattie, *Sci. Rep.* (2018) **8**, 17804.

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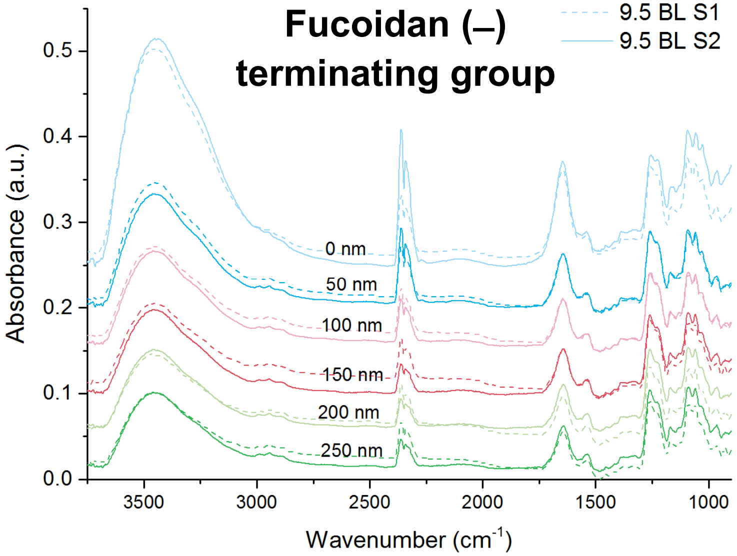
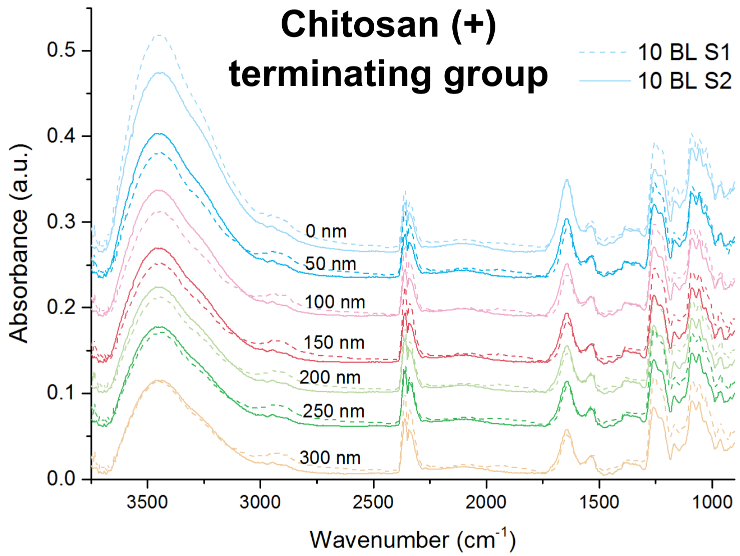
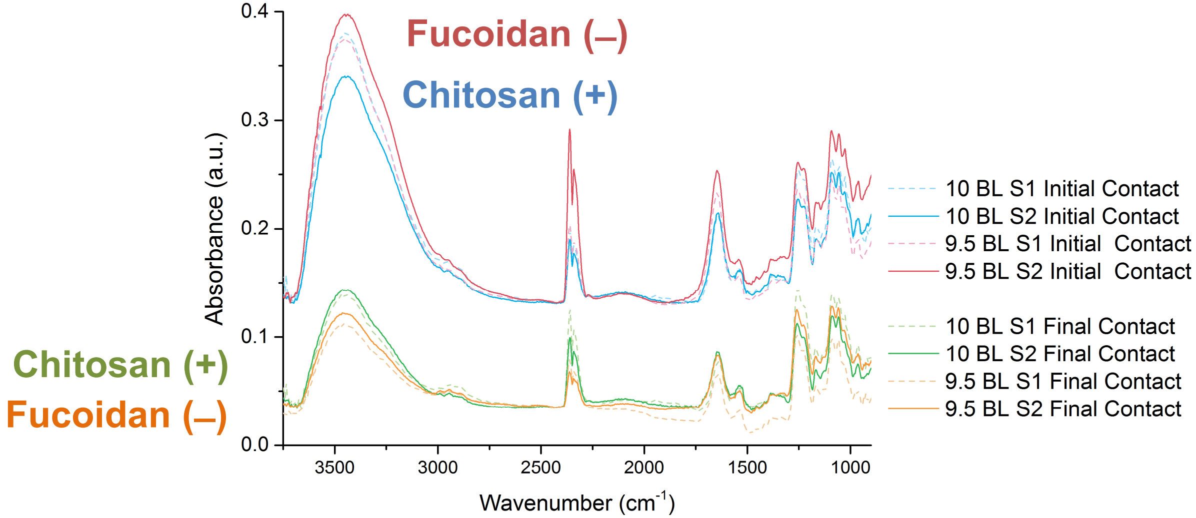
MACRO ATR-FTIR: MATERIALS & INTERFACIAL SCIENCE







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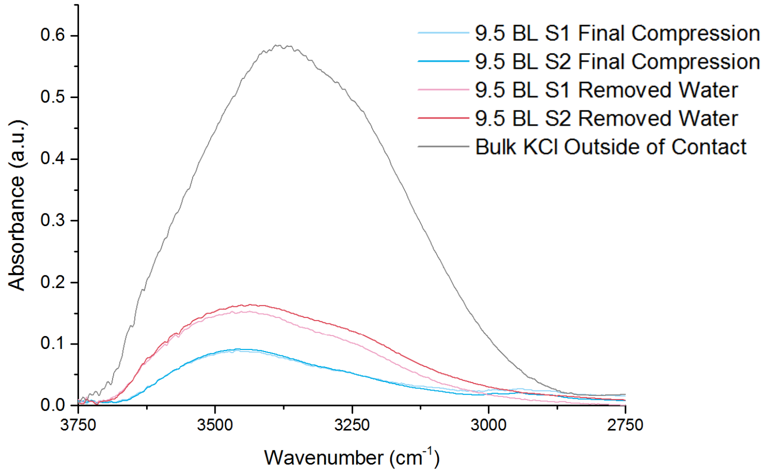
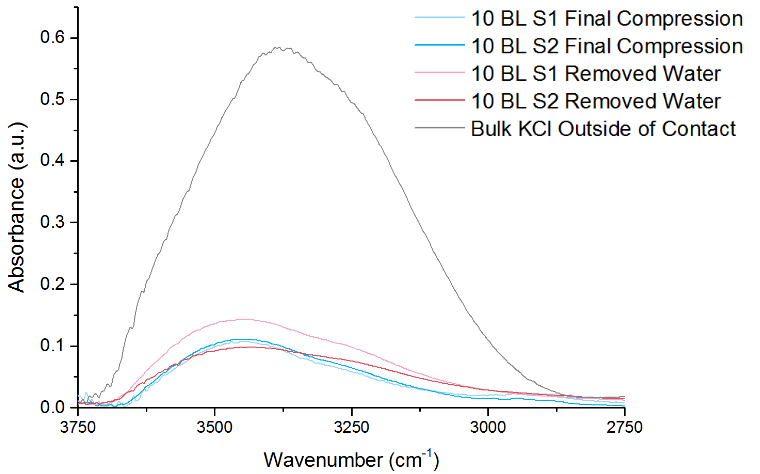
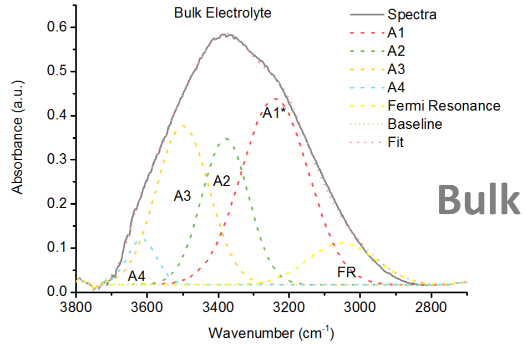
MACRO ATR-FTIR: MATERIALS & INTERFACIAL SCIENCE

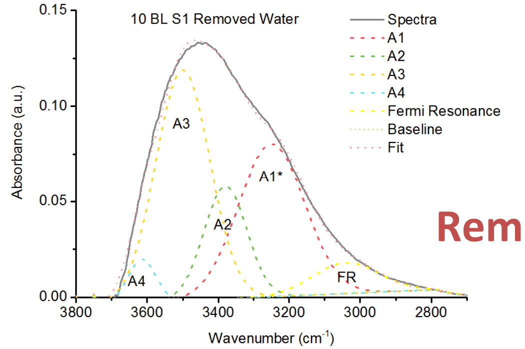
ν(O–H) Band Shape: Bulk Electrolyte *versus* Trapped Water



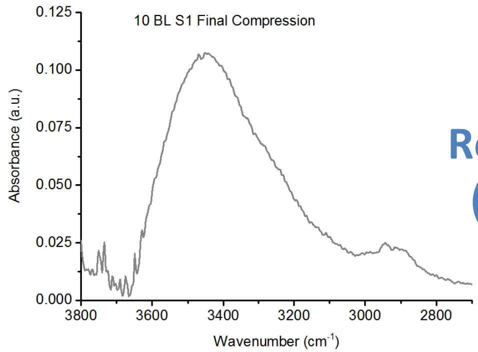




Bulk Electrolyte



Removed water



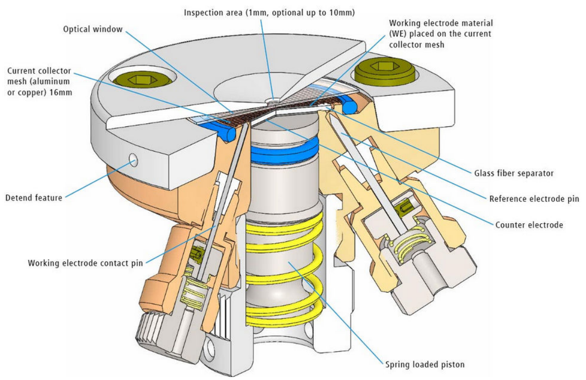
Remaining water
(pocket water)

MODEL 2B: "SOFT-CONTACT" PIEZO-CONTROLLED MACRO-ATR

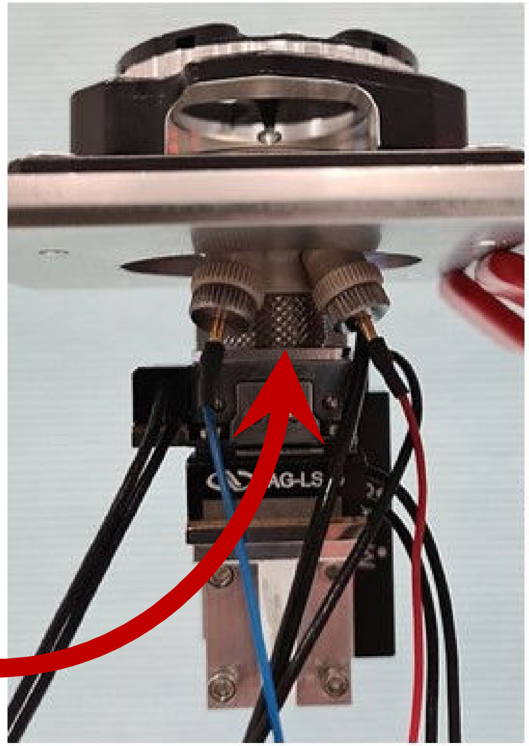
UNIVERSITY OF WOLLONGONG AUSTRALIA

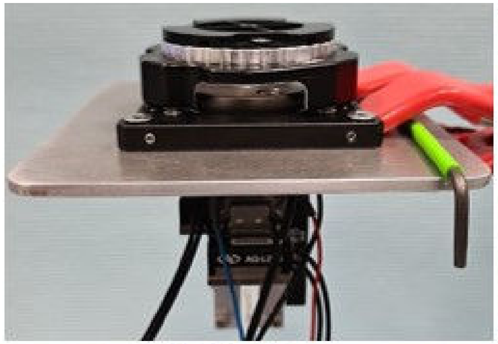
In-operando monitoring of electrochemical reaction on Zn electrode

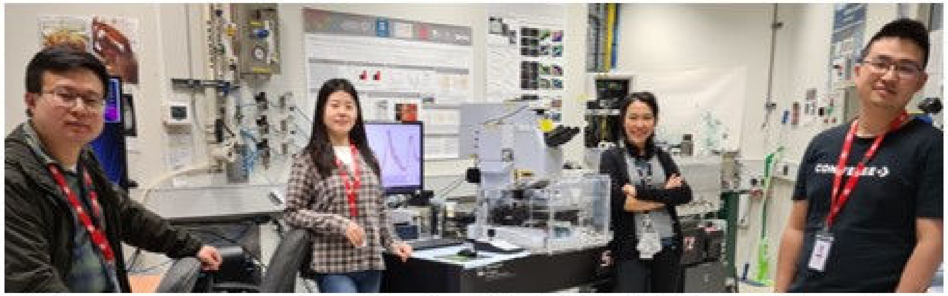
Commercial electrochemical cell (EC-CELL™)



Si ATR crystal was used in this experiment due to its inert property, and mounted in a larger magnetic cage!







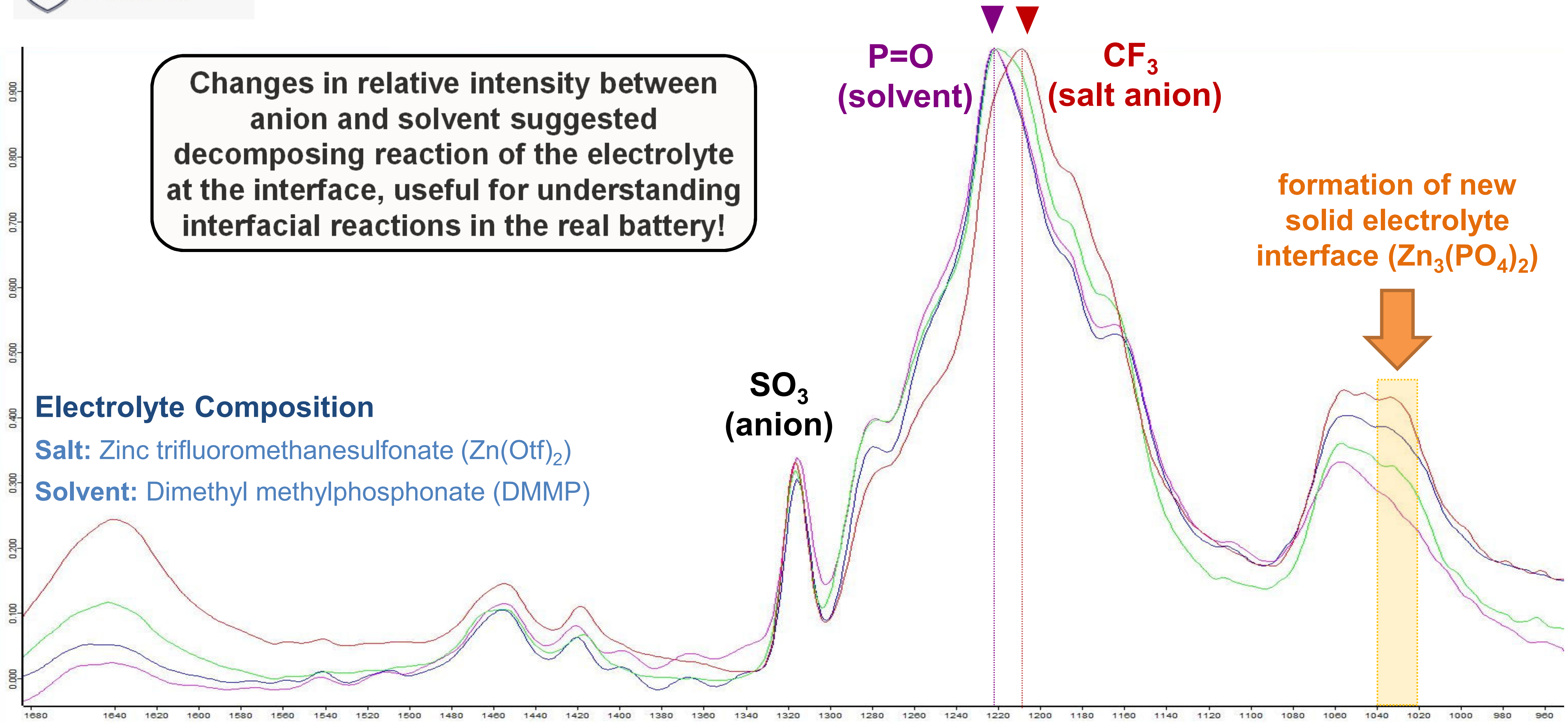
First successful experiment by the BATTERY TEAM from University of Wollongong: Zhijie, Sailin, Pimm (ANSTO) and Qining (*left* to *right*).

Supervisors: Professor Zaiping Guo & Dr. Wei Kong Pong

MACRO ATR-FTIR: ELECTROCHEMISTRY IN BATTERY RESEARCH

UNIVERSITY OF WOLLONGONG AUSTRALIA

In-operando monitoring of electrochemical reaction on Zn electrode

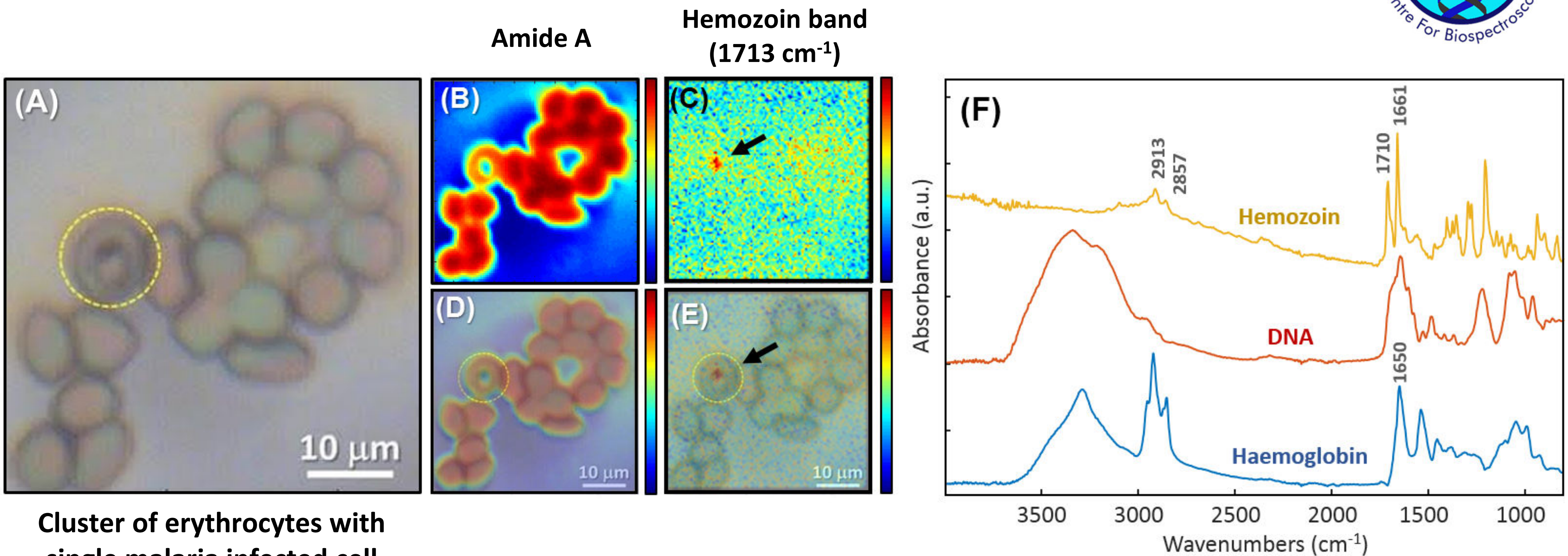


Macro ATR-FTIR Applications

BIOMEDICAL SCIENCE

MACRO ATR-FTIR: BIOMEDICAL – RED BLOOD CELL

Discrimination of *Plasmodium* malaria parasite in infected red blood cell

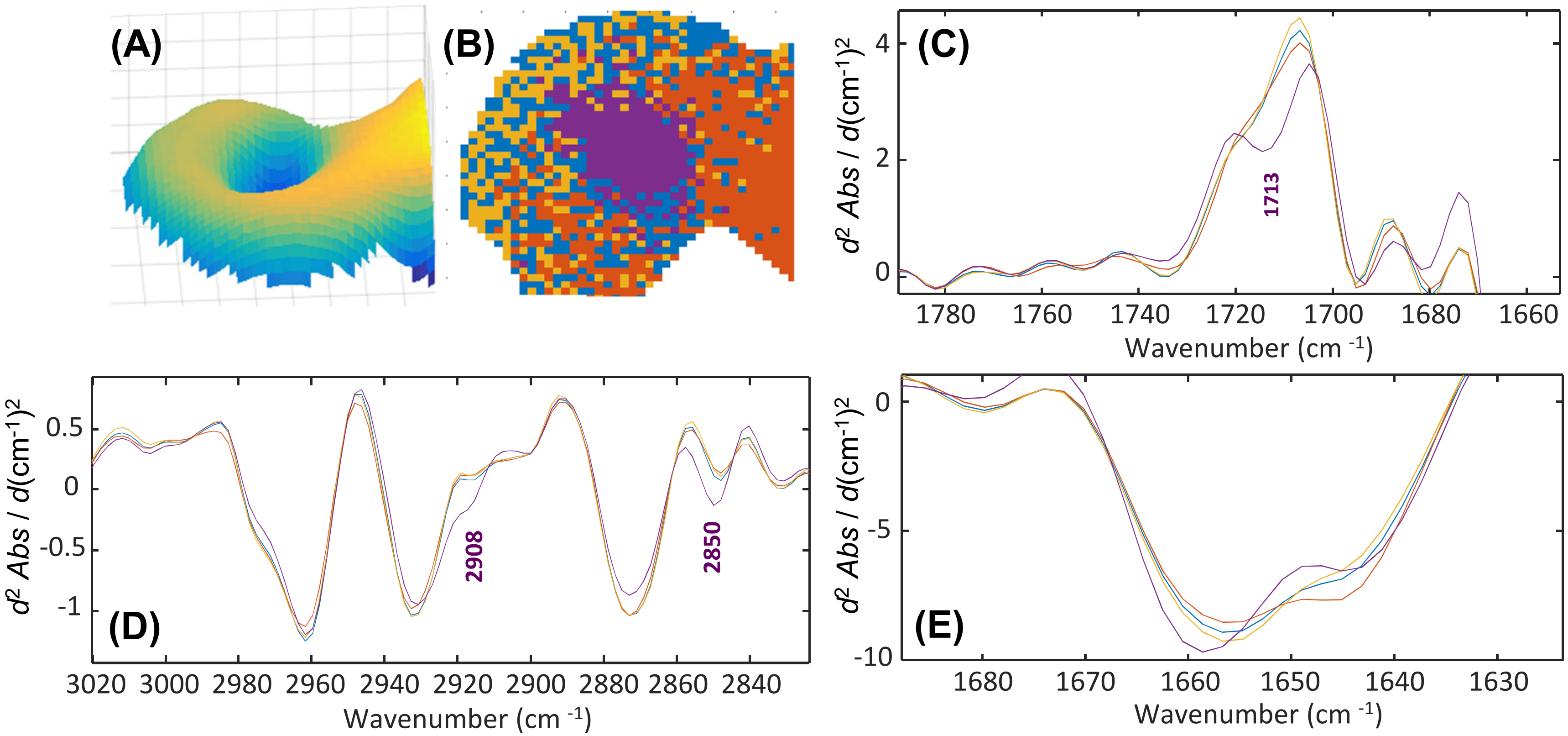


Cluster of erythrocytes with single malaria infected cell

For first time, high-resolution chemical maps of the parasite inside individual RBCs were acquired with lateral resolution smaller than the parasite itself, allowing a clear discrimination of the parasite from the rest of the cell.

MACRO ATR-FTIR: BIOMEDICAL – RED BLOOD CELL

Discrimination of *Plasmodium* malaria parasite in infected red blood cell

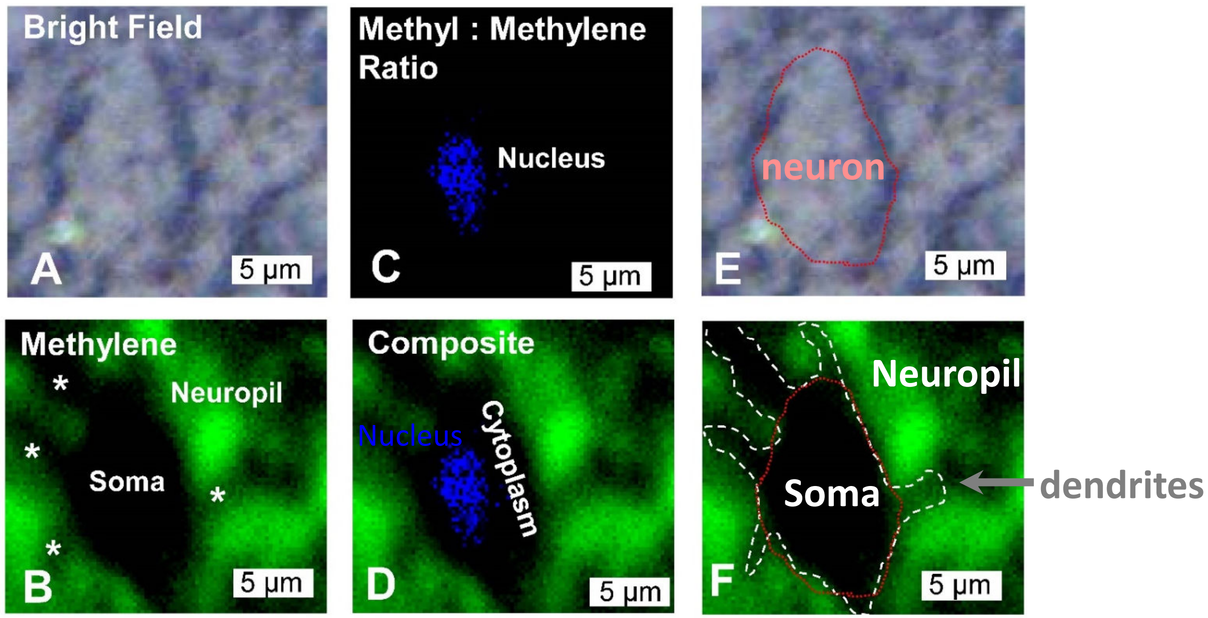


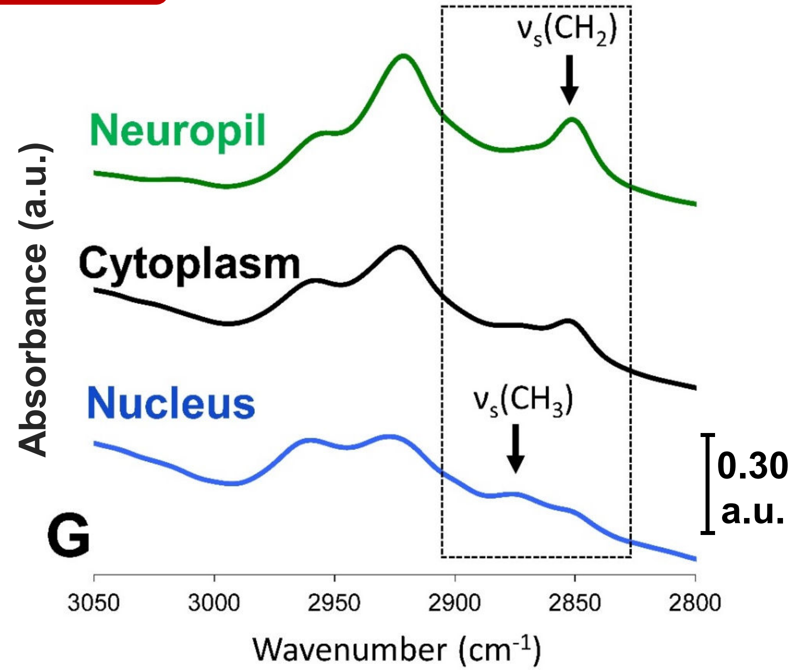
By applying cluster analysis to the chemical image of Amide I band observed for the infected RBC, a distinct class in purple indicated unique chemical makeups associated to the presence of the parasite, demonstrating the potential of the macro-ATR for studying the chemical composition of the parasites under different malaria drug treatment in the future.

MACRO ATR-FTIR: BIOMEDICAL – NEURON

Insights into lipid composition of individual neurons in brain tissue without labeling/staining requirement

Curtin University





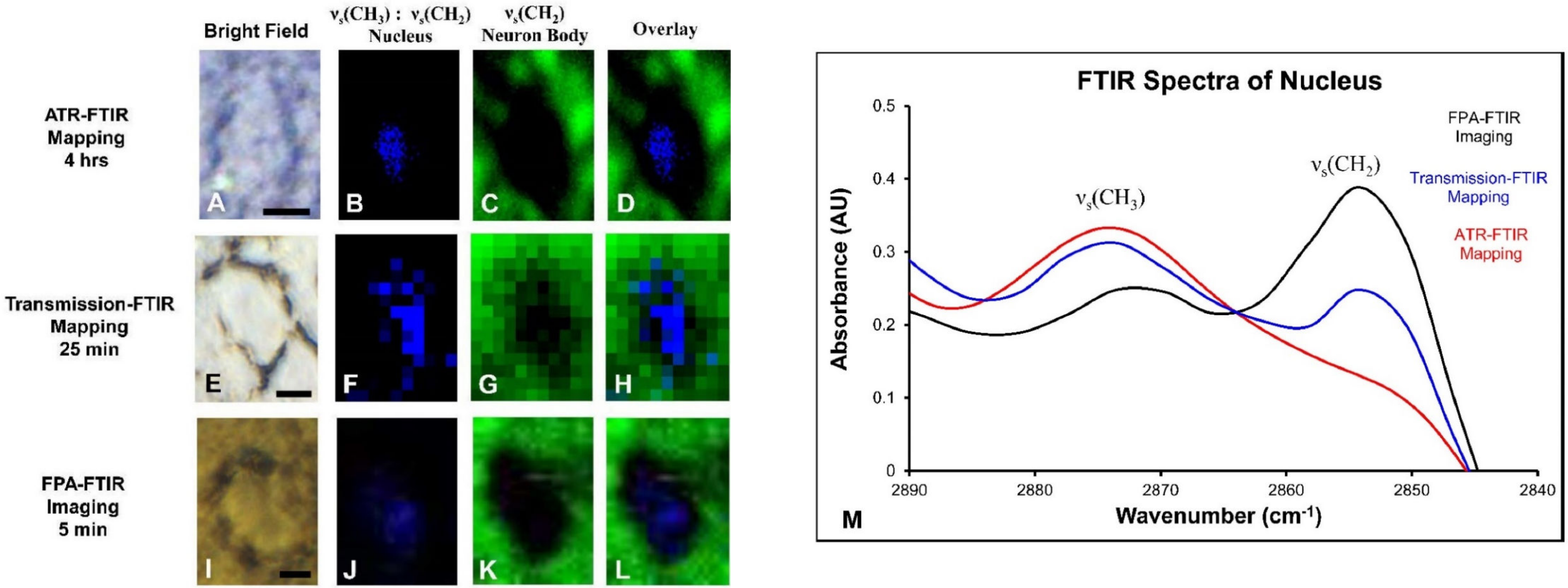
* Indicate potential locations of neuron dendrites

- **The poor image contrast in unstained brain tissue makes it difficult to identify neuron body.** Using high-resolution macro-ATR technique provide the ability to resolve the neuron location, identify the nucleus and locate thin dendrites.
- **The ability of the macro ATR-FTIR technique to directly examine the chemical composition of neurons, without using any labels or stains,** can be applied for other applications in the *neurosciences*.

MACRO ATR-FTIR: BIOMEDICAL – NEURON

Insights into lipid composition of individual neurons in brain tissue without labeling/staining requirement

Curtin University



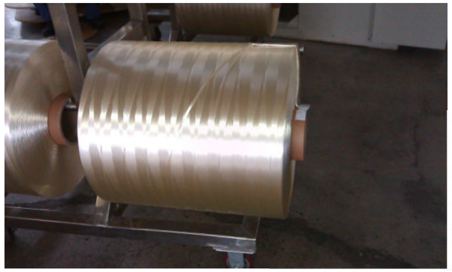
Macro-ATR technique provides (*i*) improved ability to discriminate neuron morphology and (*ii*) more accurate measure of $\nu(CH_2)$ band in the nucleus.

Macro ATR-FTIR Applications

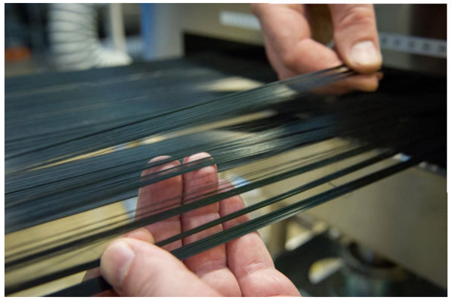
SINGLE FIBRES

MACRO ATR-FTIR: SINGLE FIBRES - CARBON

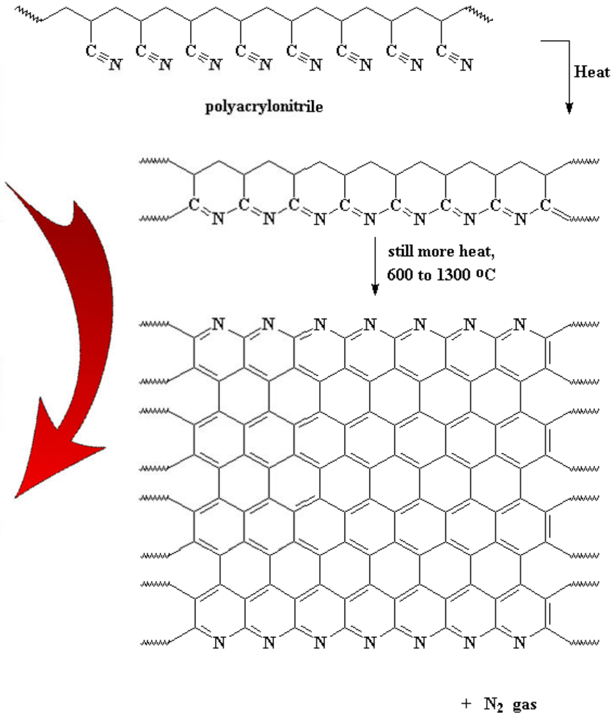
Gaining insights into heat transformation mechanism of carbon fibre production

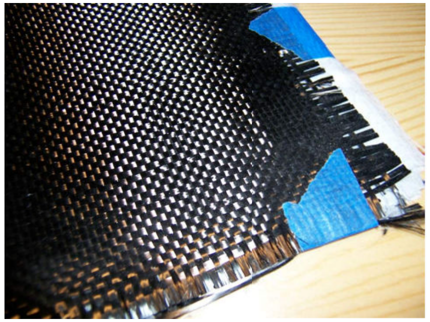


1. Polyacrylonitrile (PAN)



2. Carbon fibre

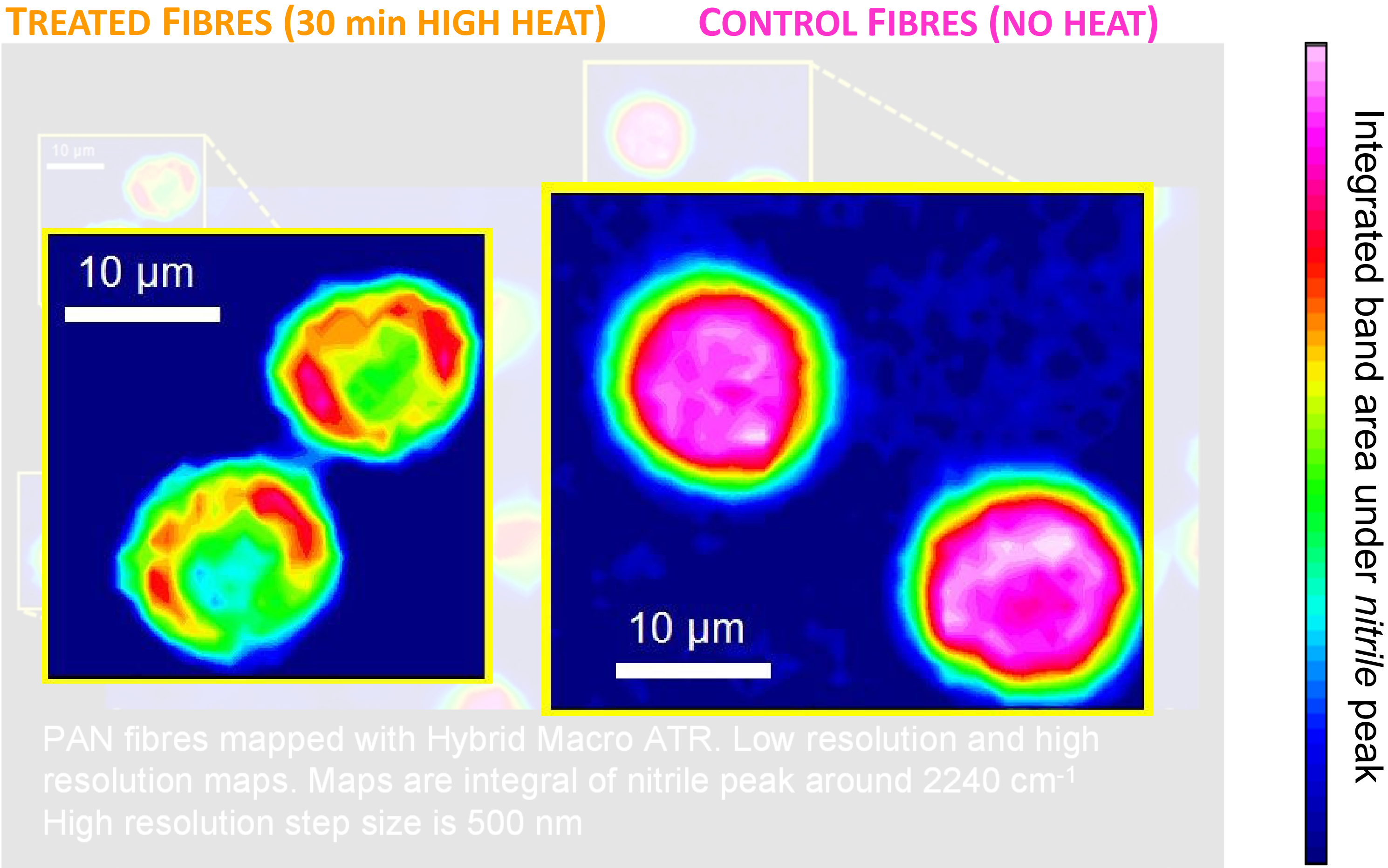




3. Woven carbon fibre

4. Carbon fibre reinforced product

MACRO ATR-FTIR: SINGLE FIBRES - CARBON



Ref [1]: S. Nunna, C. Creighton, B.L. Fox, M. Naebe, M. Maghe, M.J. Tobin, K. Bambery, J. Vongsvivut, N. Hameed, "The effect of thermally induced chemical transformations on the structure and properties of carbon fiber precursors," *J Mater Chem A*, 2017, **5**, 7372-7382.

Ref [2]: S. Nunna, M. Maghe, S. Fakhrhoseini, B. Polisetti, M. Naebe, "A pathway to reduce energy consumption in the thermal stabilization process of carbon fiber production, *Energies*, 2018, **11**, 1145.

MACRO ATR-FTIR: SINGLE FIBRES – NATURAL SILK

THE UNIVERSITY OF MELBOURNE

UNIVERSITÄT BAYREUTH

Understanding the chemical distribution of micro- and nano-fibres in a rare *Basket Web Silk*

Australian thomisid crab spider

the only spider known to weave basket web to catch prey and lay eggs

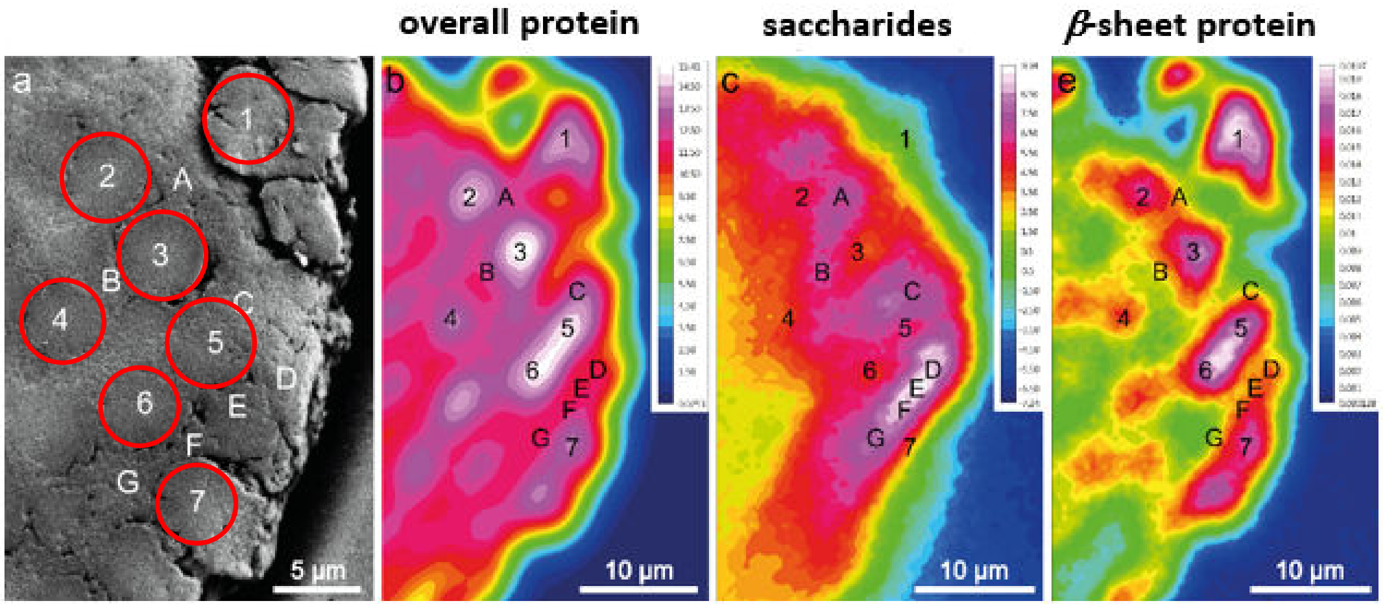
Free-standing basket web (lobster pot)

Warrumbungle National Park (NSW)

Ref: C. Haynl *et al.* Free-standing spider silk webs of the thomisid *Saccodomus formivorus* are made of composites comprising micro- and submicron fibers, *Sci. Rep.* (2020) **10**, 17624.

MACRO ATR-FTIR: SINGLE FIBRES – NATURAL SILK

Understanding the chemical distribution of micro- and nano-fibres in a rare *Basket Web Silk*



SEM

Macro-ATR chemical map of basket web cross-section

High-resolution Macro-ATR chemical maps revealed the distribution of protein, which was found to be stronger in the microfibers, and correlated well with the SEM image. The nanofibers surrounding microfibers interestingly showed stronger saccharides (C-OH and C-O-C vibration) contents, providing cohesion and thereby strength to the silk.

Ref: C. Haynl *et al.* Free-standing spider silk webs of the thomisid *Saccodomus formivorus* are made of composites comprising micro- and submicron fibers, *Sci. Rep.* (2020) **10**, 17624.

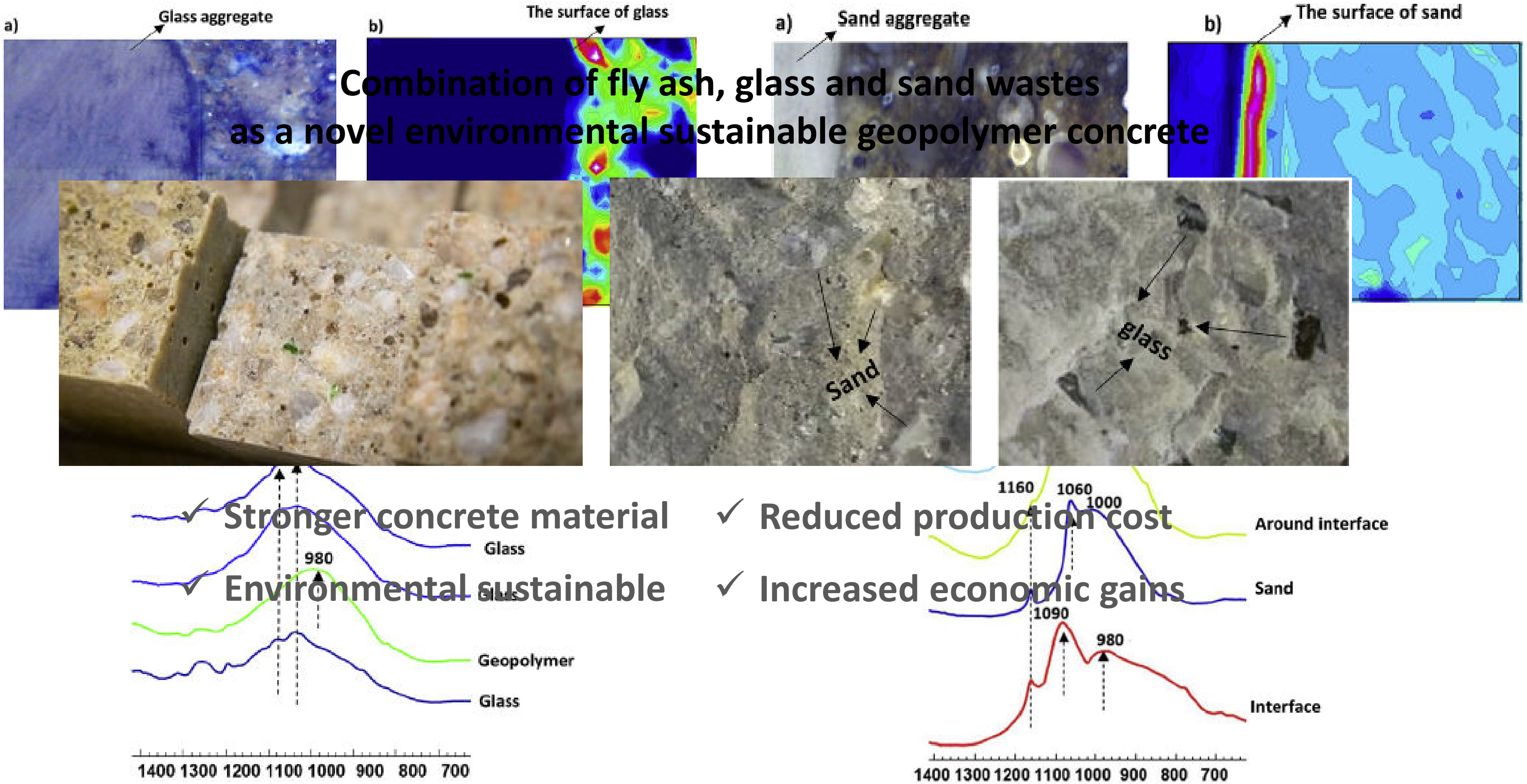
Macro ATR-FTIR Applications

COMPOSITE MATERIALS

ANSTO

MACRO ATR-FTIR: GEOPOLYMERS

Interfacial chemistry of a fly ash geopolymer with glass and sand aggregates used as geopolymer concretes in construction industry



Combination of fly ash, glass and sand wastes as a novel environmental sustainable geopolymer concrete

- ✓ Stronger concrete material
- ✓ Environmental sustainable
- ✓ Reduced production cost
- ✓ Increased economic gains

Ref: A. Hajimohammadi, *et al.* High strength/density ratio in a syntactic foam made from one-part mix geopolymer and cenospheres, *J. Cleaner Production* (2019) **231**, 980-989.

MACRO ATR-FTIR: POLYMER COMPOSITES

SWINBURNE UNIVERSITY OF TECHNOLOGY

Effect of prolonged UV and humidity exposure on silica nanoparticle-embedded polyester coated steel surfaces

BLUESCOPE

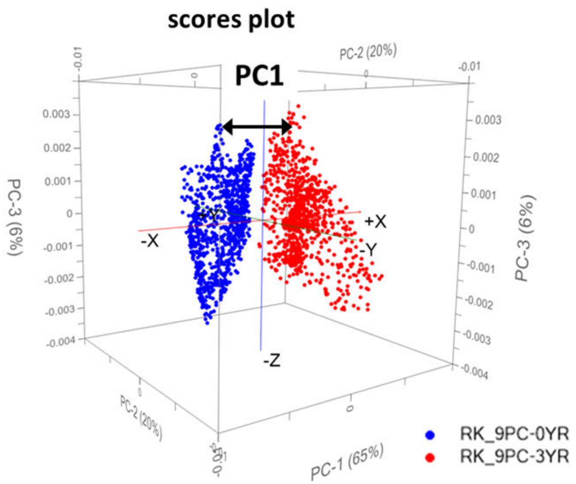
Colorbond®

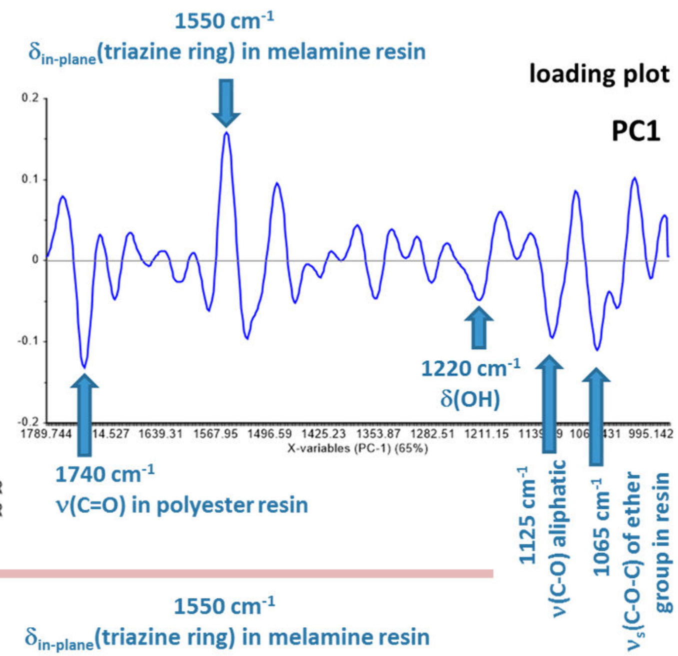
Ref: J. Vongsvivut, V.K. Truong, M. Al Kobaisi, S. Maclaughlin, M.J. Tobin, R.J. Crawford and E.P. Ivanova, *PLOS ONE*, 2017, **12**, e0188345.

ANSTO

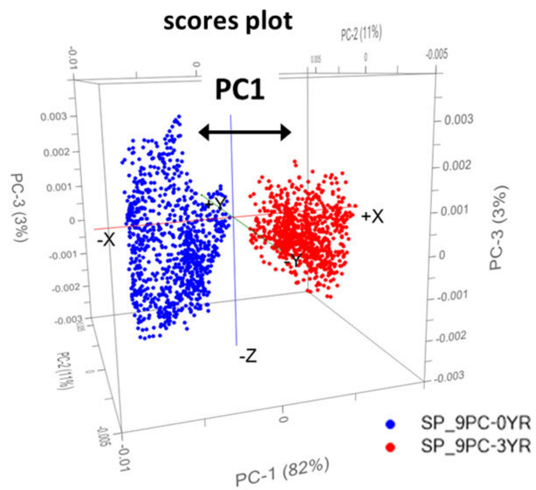
SiO_2NPs 9%

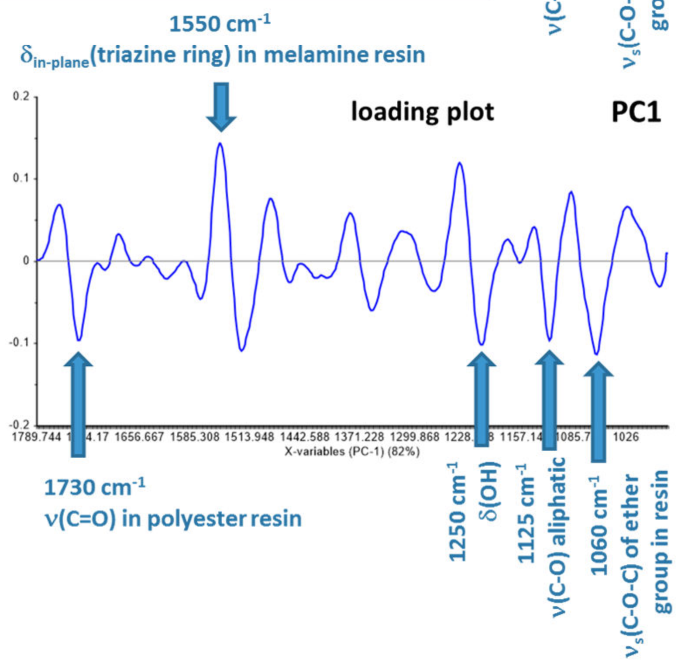
Queensland





Singapore





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