

The Australian Synchrotron - A powerful tool for chemical research available to New Zealand scientists

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Introduction

The Australian Synchrotron began operation in 2007 and provides outstanding opportunities for chemical researchers in New Zealand. There are ten beamlines that provide techniques to suit many different types of research, including several of interest to chemists and chemical engineers. Easy access to this synchrotron facility gives New Zealand science a boost and enables the use of some of the latest and best methods that exist. This article gives a snapshot of some of the techniques available, illustrating them with examples from recent work.

The synchrotron should perhaps be better thought of as the Australasian Synchrotron, since a portion of the funding for construction of the initial suite of beamlines and for operation comes from New Zealand. The initial funding was from the state government of Victoria, and there were contributions from many of the major Australian universities, the Australian Nuclear Science and Technology Organisation (ANSTO), CSIRO and the Government of the Commonwealth of Australia. New Zealand also contributed: the New Zealand Government matched the funding provided by the major New Zealand universities and some of the Crown Research Institutes. Altogether New Zealand contributed A\$5 million to the construction cost of A\$221 million, with an additional contribution of A\$5 million to operational costs.

The ownership of the Australian Synchrotron is vested in a company in which the contributors to the facility hold shares, a convenient way to define ownership. The contributors from New Zealand hold shares in the company through the vehicle of the New Zealand Synchrotron Group Ltd (NZSG). In October 2012, the management of the Australian Synchrotron passed to Synchrotron Light Source Australia, a wholly-owned subsidiary of ANSTO.

Gaining scientific access to the synchrotron is rather simple and those who are allocated time through the competitive application process not only get to use a beamline, but currently, their airfares to Melbourne are paid and there is free accommodation on-site for up to three experimenters. Three times a year there is a call for proposals when applicants submit an outline of the science they would like to do, with details of the experiment(s). Each beamline has a designated panel of experts that assesses the proposals, assisted by anonymous reviewers, so that the available beamtime is allocated to the best proposals. The use of the Australian Synchrotron by New Zealand-based researchers has grown steadily (Fig. 1). This has been assisted by 'foundation investor' time, which is a fixed allocation of time to each of the organisational groups that funded the construction of the synchrotron. This beamtime does not

undergo the usual merit assessment and has enabled new and inexperienced users to obtain easy access to the synchrotron.

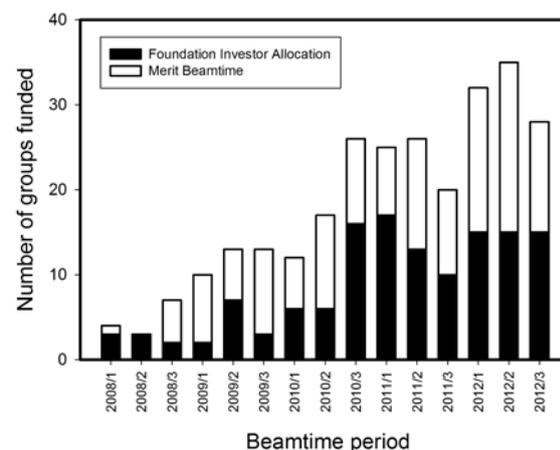


Fig. 1. New Zealand-based user access to the Australian Synchrotron.

Experiments at the synchrotron are supported by a team of beamline scientists for each beamline. The beamline scientists provide expert help for all experiments, and should always be consulted by users prior to submitting a proposal. These scientists not only keep the beamlines running in optimal condition, but they are constantly improving, adding to and developing the beamlines. My experience of the beamline scientists has been excellent – nowhere have I met such a helpful, dedicated and knowledgeable group of scientists who want to ensure that my experiments work. Although the physical equipment is state-of-the-art and of very high quality, the beamline scientists are the key to the success of this large science facility. The culture is very much one of “can-do” and “we will make it easy for you”, and it extends to other support staff at the Australian Synchrotron, many of whom were scientists before they stepped into administrative or support roles and who, therefore, have an understanding of the users.

There are ten beamlines. Four are based on diffraction – Powder Diffraction (PD), Small and Wide Angle X-ray Scattering (SAXS/WAXS), Molecular Crystallography (two beamlines MX1 and MX2); three are based primarily on spectroscopy – X-ray Absorption (XAS), Far Infrared and High Resolution Infrared (FIR/HRIR), Soft X-rays (SXR); and three are primarily imaging techniques or spectroscopy based imaging – Imaging and Medical (IM), Infrared Microspectroscopy (IRM), X-ray Fluorescence Microscopy (XFM). The beamlines most heavily used by New Zealand-based researchers are MX (75 groups in 2011-2012), followed by SAXS (32), with moderate use also of SXR (15), XAS (14), PD (14) and IRM (12). Less

use has been made of XFM (5) and FIR/HRIR (3). Examples from two spectroscopy and two diffraction beamlines are given in the discussion that follows.

X-ray Absorption Spectroscopy Beamline – XANES and EXAFS

The X-ray Absorption Spectroscopy (XAS) beamline was apparently the first to record data from a sample at the Australian Synchrotron. There was already an established base of knowledgeable users in XAS as a result of the Australian National Beamline Facility being established at the Photon Factory in Japan in 1992. That facility now consists of a dedicated XAS beamline that is equipped and staffed by Australians; it will close in 2013.

There are two techniques that have been usually used on this beam line – X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Spectroscopy (EXAFS). The first of these gives chemical information (especially oxidation state) and, in simple terms, is often used for a “fingerprint” identification of chemical environments. The second technique gives structural or crystallographic information and is, therefore, a cousin to the diffraction methods, although it is element-specific and does not necessarily require long range crystal order.

The basis of XAS is a scan of the X-ray energy across an absorption edge for the element of interest and measuring either the absorption of the X-rays by the sample or the fluorescence from the sample. The technique is, therefore, specific to the element for which the edge has been chosen and is applicable to a wide range of elements. It is difficult to create a sufficiently intense, tuneable X-ray source for a small-scale laboratory instrument so XAS is mostly performed at synchrotron facilities, although laboratory based instruments are available.¹

An example where XANES has been useful is in the study of metal nanoparticle formation in plants. Trace metal concentrations in plants have long been used in geoprospecting² and it has long been known that some plants can hyperaccumulate metals,³ even to the extent that concentrating precious metals has been proposed as a method for phytomining.⁴ More recently the prospect of using plants to produce metal nanoparticles for applications such as catalysts has been proposed.

The accumulation of various precious metals in plants, both land plants and microalgae has been studied. While transmission electron microscopy combined with energy dispersive spectroscopy can identify that the precious metal elements are present as small particles in the plants (Fig. 2),⁵ XANES is able to determine the chemical state of the elements present.⁶⁻⁷ For example, gold in the metallic state can be distinguished from various gold salts (Fig. 3). Combined with a similar study of the deposition of various other precious and semi-precious metals, this has also enabled the redox environment and capacity of plants to be inferred.⁷

EXAFS, which involves a transformation of the absorption spectra, recorded to well past the absorption edge energy, provides a distribution of distances from the element

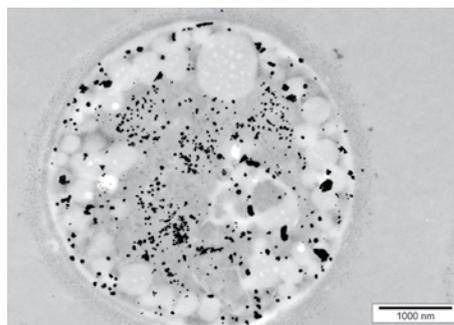


Fig. 2. Transmission electron micrograph of an unstained section of the microalga *Chlorella vulgaris* containing Au nanoparticles (dark spots).

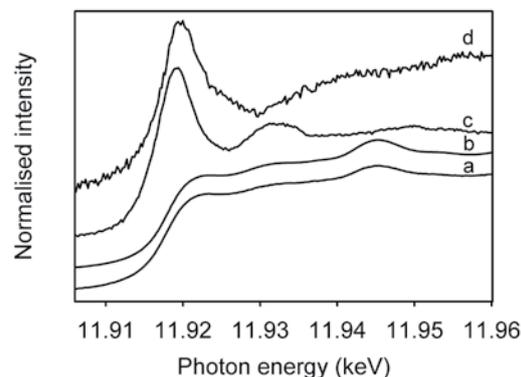


Fig. 3. XANES spectra of a) Au foil, b) *Chlorella vulgaris* containing Au nanoparticles, c) HAuCl_4 , d) $\text{Au}(\text{OH})_3$. Reproduced from reference 6.

of measurement to its nearest neighbours. For example, in the mixed oxide of iridium and ruthenium,⁸ which is a very good electrocatalyst for oxygen evolution, it is possible to determine the spacing of the atoms around each atom of the element of the chosen absorption edge. An example for Ru is shown in Fig. 4.

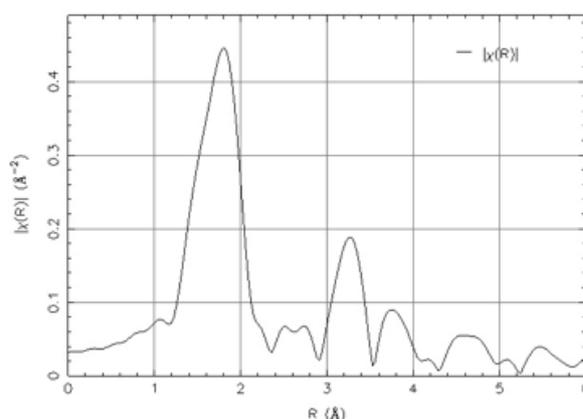


Fig. 4. Radial distribution function obtained from EXAFS of Ru in $(\text{Ir}_{0.75}\text{Ru}_{0.25})\text{O}_2$ (Samples produced by Owe and Sunde as in reference 8). Data processed using ATHENA (reference 19).

Soft X-ray Beamline – XPS and NEXAFS

The Soft X-ray (SXR) beamline operates in the energy range 100 – 2500 eV. At this energy X-rays are strongly absorbed by air and, therefore, the path of the X-rays, from the source to detector, including the sample environment, needs to be in a vacuum. The two techniques that use this beamline are X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS).

For the technique of XPS, a fixed-energy X-ray source is incident on a sample and the energy spectrum of the excited electrons ejected from the sample (photoelectrons) is recorded. The soft X-rays penetrate only a short distance into the sample and the electrons ejected can escape only from even closer to the surface, making this a surface-sensitive technique. Each element present in the sample emits electrons with a series of energies characteristic of that element. It is possible to obtain quantitative measurements (within a few percentage points) of the elemental composition of a surface. The precise energy of peaks in the photoelectron spectrum depends on the chemical environment of the element, so that the position of these peaks may shift for different chemical states. The shift in energy can sometimes be quite substantial (several eV). It is therefore possible to get some information about the chemical states on the surface. It is also possible to quantify the proportion of each chemical state for a particular element, by deconvoluting a complex peak (sometimes the peaks are quite separate) and measuring the areas under the peaks. Good books about XPS include one by Briggs and Grant.⁹

One of several advantages of synchrotron-based XPS is that it is not constrained by a single X-ray energy – normally the case for a laboratory-based instrument (typically with an Al or Mg anode as an X-ray source). One reason this is an advantage is that the depth of analysis depends on the energy of the photoelectrons: higher energy electrons exit from a greater average depth. The kinetic energy of the photoelectrons (E_k) depends on the binding energy of the electron with the atom (E_B), and the X-ray energy incident on the atom ($h\nu$) in this way: $E_k = h\nu - E_B - \phi$, where ϕ is the surface work function. Therefore, by choosing the appropriate X-ray energy, it is possible to dictate the photoelectron energy and thus the analysis depth (for a particular photoelectron peak).

This ability to choose the analysis depth is particularly pertinent to the study of nanoparticles. Nanoparticles are of interest in many fields and one fairly recent development is the production of core-shell nanoparticles, in which a thin layer of one substance coats a core of a different material. These find application, for example, in catalysis and photonics. Synchrotron-based XPS can be used to measure the elemental composition and chemical state at various depths in these nanoparticles by varying the X-ray energy (and therefore the photoelectron energy and escape depth). In contrast to this 'energy resolved' method available only at synchrotron sources, the two alternative methods of XPS-based depth profiling that are used on flat surfaces, viz., angle-resolved depth profiles and ion sputtering to etch the surface between analyses, that are the only ones available in the home laboratory, are not much use on nanoparticles.

A specific example of the use of Synchrotron-based XPS on core-shell nanoparticles has been the analysis of a core-shell electrocatalyst designed for oxygen evolution.¹⁰ The core is antimony-doped tin oxide (ATO; the antimony doping gives the tin oxide ionic and electrical conductivity), and the shell consists of an active catalytic material containing a mixture of IrO₂ and RuO₂, created

to achieve the superior catalytic activity of RuO₂ while retaining the superior stability of IrO₂.¹¹ By selecting X-ray (photoelectron) energies of 100 eV, 350 eV, and 1400 eV, it was possible to analyse for elemental and chemical composition at the approximate depths of 0.5, 1 and 2 nm. The example shown (Fig. 5) demonstrates the difference in the chemical state of Ir at different depths (for a range of samples that had undergone different heat treatments).

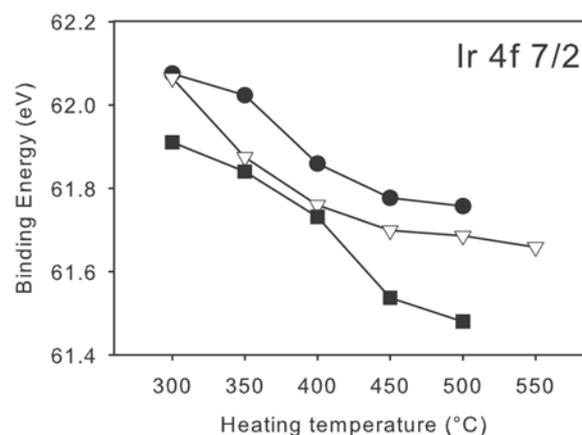


Fig. 5. Electron binding energies for Ir 4f7/2 on core-shell particles at different analysis depths. Circles 100 eV photoelectron energy; triangles 350 eV photoelectron energy; squares 1400 eV photoelectron energy. Adapted from reference 10.

NEXAFS is another technique available on the Soft X-ray beamline. Despite the similarity of the acronym, it is not EXAFS; rather it is more akin to XANES (an easy way to remember this is that NEXAFS could be the abbreviation for "Not EXAFS").¹² NEXAFS is used for analysing light elements on surfaces (light elements have strong absorption edges in the soft X-ray region). NEXAFS is most often applied to carbon, and the resulting spectra depend on both composition and orientation. NEXAFS¹³ (and XPS)¹⁴ have been used to study the formation of fluorocarbon films on graphite anodes that can develop during the aluminium smelting process. Both techniques were able to identify a partially fluorinated carbon film forming on the surface under very high overpotential conditions. NEXAFS has an advantage over XPS in that the spectrum produced is very orientation dependent if the sample's surface structure is anisotropic and is, therefore, able to give some structural as well as chemical information. For example, the orientation of graphite on the surface of the carbon anodes used in the aluminium electrode study was readily apparent.¹³

Powder Diffraction Beamline

In X-ray powder diffraction (PD), a powdered crystalline or partially crystalline material is irradiated with a monochromatic X-ray beam and the diffraction pattern recorded, i.e., the angles and intensities of the diffracted X-rays are recorded. The basic technique dates back to Debye and Scherrer from about 1916 and builds on the work of the Australian physicist Bragg from 1912. The technique can provide very precise information about the structure of crystalline materials – the positions of atoms in a unit cell, the distortions present in the structure and the crystallite size.¹⁵

The PD beamline at the Australian Synchrotron has many advantages over typical laboratory-based systems. The key advantages arise from the very high X-ray flux possible; very high resolution (owing to very precise measurement of the diffraction angle, itself a result of a monochromatic, highly collimated beam); the ability to choose the X-ray energy (to balance absorption effects and resolution requirements); rapid data collection owing to the type of detector employed; and the ability to use high-energy X-rays and therefore high q for experiments involving total scattering analysis. The wavevector, q , depends on X-ray wavelength, λ , and scattering angle, θ , by the relationship $q = 4\pi \sin \theta / \lambda$.

Because of the high resolution possible, small changes in crystal structures can be accurately measured, and the good signal-to-noise ratio enables a small amount of a particular component in a mixture to be detected. The detector that allows rapid collection of high-resolution diffraction patterns simultaneously records the diffraction intensity over an angle of 80° to an intrinsic resolution of 0.0004° . To measure a larger angular range, the detector needs to be moved once. This means that it is possible to measure metastable systems or fairly rapidly changing processes during, for example, heating or chemical reactions. A diamond anvil cell is also available and enables studies of pressure effects on crystal structure.

An example where these features have been exploited was in a study of a series of mixtures of IrO_2 and RuO_2 . The electrochemical behaviour of the materials had been characterised and related to the structure. PD revealed that they consisted of single-phase materials except for one mixture, which had a small portion of a second component⁸ (Fig. 6). It was also possible to accurately determine the shift in the lattice parameters with the change in composition (Fig. 7), showing that as Ru is added the unit cell contracts in the c -axis.

The ability to use high-energy X-rays at high flux enables analysis of the pair distribution function (PDF) of a total scattering spectrum. PDF is a powerful technique for nanostructured materials that lack a high level of crystallinity.^{16,17} The data processing involves a Fourier transform of the scattered X-ray intensity with wave vector. It produces a pair distribution, which is a probability distribution of the distances between pairs of atoms in the material (Fig. 8). The PDF of a structure can also be calculated *a priori* so that experimental data can be compared with a structural model or the model fitted to the data (Fig. 8).

In order to get a good PDF, it is necessary to measure the scattered intensity to a high level of q , i.e., high angle and short wavelength and to get good counting statistics, including at high q . Synchrotron radiation is ideal for this. Typically, a home laboratory source will use $\text{Cu K}\alpha$ radiation, which has a wavelength of 1.54 \AA (although Ag or Mo sources that produce shorter wavelengths are available). However, on the PD beamline at the Australian Synchrotron, X-rays at high intensity of 21 keV (0.59 \AA) can be obtained. This energy is sufficient to obtain data suitable for PDF analysis. PDF measures pairwise distribution, av-

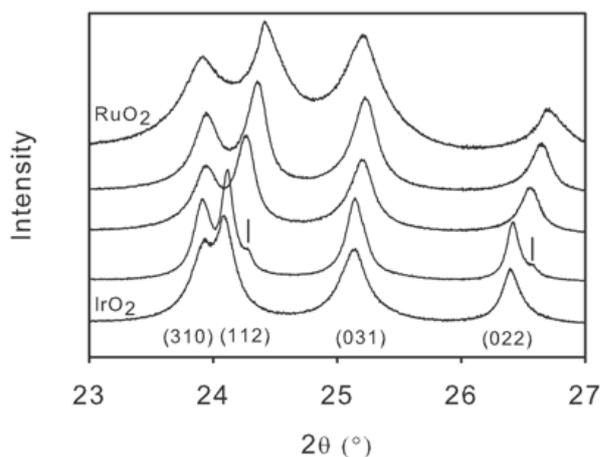


Fig. 6. A portion of the X-ray diffraction patterns for $\text{Ir}_{1-x}\text{Ru}_x\text{O}_2$ heated to 600°C ($x < 1$) and RuO_2 heated to 500°C for (offset patterns, bottom to top) $x = 0, 0.25, 0.5, 0.75$ and 1 . Vertical bars indicate shoulders on pattern for $\text{Ir}_{0.75}\text{Ru}_{0.25}\text{O}_2$. Miller indices indicated below peaks. Reproduced from reference 8.

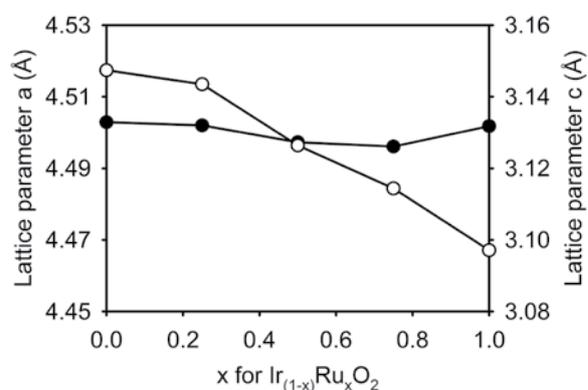


Fig. 7. Lattice parameters a (\bullet) and c (\circ) obtained by Rietveld refinement of powder diffraction data for compositions in the range $\text{Ir}_{1-x}\text{Ru}_x\text{O}_2$. Adapted from reference 8.

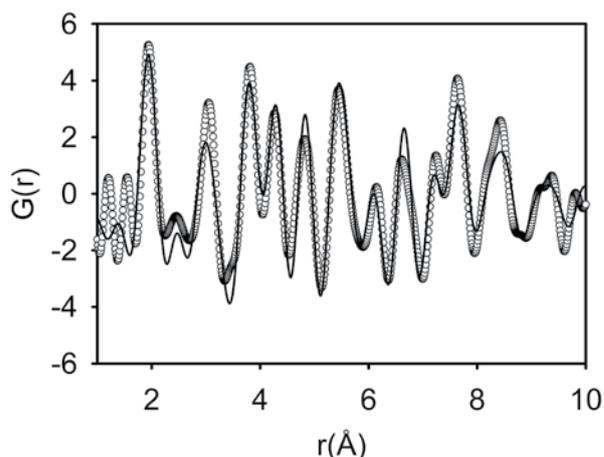


Fig. 8. PDF of nanocrystalline anatase TiO_2 . Circles are the PDF calculated from data; The solid line is calculated PDF from an adjusted model of anatase. Data processed using PDFGetX2 (see reference 20), modelling performed using PDFGui (see reference 21).

erage atom to atom lengths, rather than distances determined from average lattice positions (which is the case in conventional X-ray PD). For some structures, these are not the same. A more detailed description, with some interesting examples, is in the book by Egami and Billinge.¹⁷

Small Angle X-ray Scattering Beamline

Small Angle X-ray Scattering (SAXS) is another scattering technique but one that measures very small scattering angles. It is, therefore, suitable for very different samples compared to those appropriate for the PD beamline. Scattering at small angles provides information about larger structural features than does the PD beamline. It is commonly applied to solid polymer materials (both biopolymers – such as proteins – and engineering polymers) and to nanoparticles and polymers in suspension.

The SAXS/WAXS beamline at the Australian Synchrotron has a very good Pilatus detector that captures a full 2D scattering pattern. For studies of aqueous suspensions, the pattern obtained is likely to be the same at all azimuthal angles, so that the 2D capability of the detector is not fully used. Instead, the scattering pattern is normally converted to a single I versus q plot as the first step in the data processing. However, for solid materials, the anisotropic nature of the material can be fully analysed, possibly yielding quite complex scattering patterns.

For samples suspended in liquids, typically one might be interested in the shape or conformation of a macromolecule in this environment, and SAXS can provide this information. The technique can be complementary to analysis on the MX beamline, which is typically used for determining the full structure of a macromolecule that has been successfully crystallised. It is also possible to obtain shape and size distribution information from SAXS for nanoparticles in suspension.

SAXS is a technique that is available in home laboratory instruments; however, SAXS at the Australian Synchrotron has several advantages. The combination of the high X-ray flux and very sensitive detector enables very rapid acquisition of full spectra (of the order of a second) so that it is possible to monitor reactions that take place over a few minutes or hours. Also, the X-ray beam can be focussed to a minute spot on the sample, typically 250 x 80 μm , enabling mapping of the structure of an inhomogeneous material (as are many natural materials).

For solid samples, it is possible to apply stress to the sample while it is being exposed to SAXS and observe the material's structural behaviour while under stress. We have built a device for stretching leather and biological tissues on the SAXS beamline while recording scattering patterns and used the results to improve our understanding of the average structure, the variation of structure through the tissue and the deformation behaviour under stress. Although so far only a portion of the information contained within the diffraction patterns has been used, this technique has been very revealing of structure-function relationships. More specifically, the relationship between ovine and bovine leathers and strength has been found to be due in large part to the orientation of the collagen fibrils.¹⁸ The orientation can be easily seen in the diffraction patterns (Fig. 9) and can be quantified as an orientation index. The d -spacing of collagen can be used as an internal strain gauge in collagen materials to help to understand how the forces are transmitted and accommodated within a material as it is strained. For example, when leather is being

stretched, often the fibres first rearrange to become more aligned and then the individual fibrils begin to stretch as seen by the increase in the d -spacing (Fig. 10).

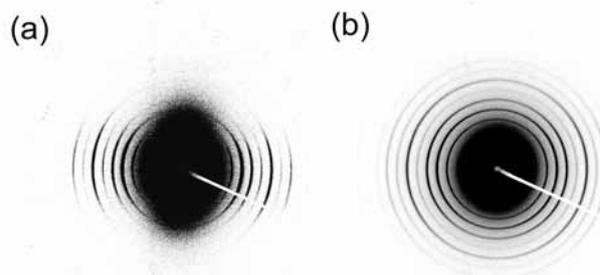


Fig. 9. SAXS scattering pattern of; a) leather with aligned collagen fibrils, b) leather with a more isotropic arrangement of collagen fibrils. The rings are due to the collagen d -banding (the rings are different reflection orders of the same structures). The distance from the centre (equatorial angle) is due to d -spacing, the variation around the rings (azimuthal angle) is due to the alignment of the fibrils.

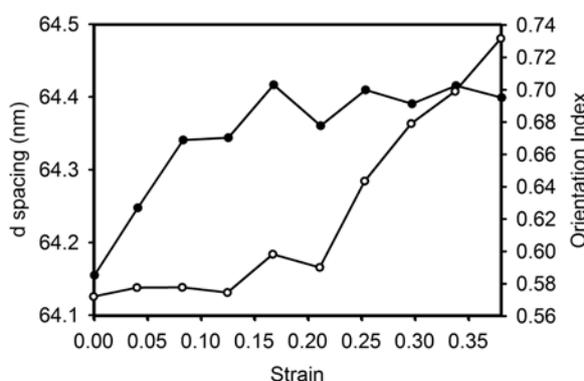


Fig. 10. Stretching of ovine leather d -spacing and orientation measured edge-on versus strain: (○) d -spacing and (●) orientation index. Reproduced from *J. Agric. Food Chem.* (2012) **60**, 1201–1208 ©American Chemical Society.

Concluding remarks

The Australian Synchrotron is a state-of-the-art, world class facility right on our doorstep. Access is generously facilitated by the NZSG and supported by expert and helpful beamline staff. Just four of the beamlines, and only some aspects of the techniques available, have been outlined briefly here, but the hope is that this article has conveyed some of the powerful capability of the Australian Synchrotron for chemical research and will stimulate further enquiry and interest.

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Much of the work described in here was performed at the Australian Synchrotron – on one of four beamlines: the SAXS, PD, XAS and SXR. Dr Don Smith of the NZSG provided the AS usage data. Katie Sizeland, from Massey University, assisted with figure preparation and provided useful advice. Prof Jim Metson, from the University of Auckland, gave helpful advice on the content.²² Sue Hallas of Nelson edited the manuscript.

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