AXAA

Australian X-ray Analytical Association

Newsletter Issue 2 2023

President's Address

Dear AXAA members and friends,

Welcome to the second issue of the AXAA newsletter in 2023.

I would like to start by sharing a summary of our recent Awards Dinner on Monday 21st August. With so many members in one place for the IUCr meeting we used the opportunity to put on a long overdue celebration!

The day commenced with an engaging ICDD Workshop, where participants dove into the ICDD Powder Diffraction File PDF® databases and MDI JADE®Pro software. This session was informative but also very hands-on, allowing us to get a feel for the different options to search.

In the afternoon, distinguished speakers shared their insights on a wide range of topics, from neutron scattering studies to XRF spectrometry, and from incorporating machine learning into XRF datasets to the fascinating world of micro-CT applications in Australian amber. The depth of knowledge and the diversity of subjects discussed truly showcased the richness of our community's expertise.

Following the day's sessions, we transitioned to a relaxed networking hour, generously sponsored by Diffraction Technology.

The AXAA Awards Dinner (sponsored by CSIRO), was our opportunity to honor our colleagues who have made significant contributions to X-ray and neutron sciences. It was especially heartwarming to see Nathan Webster finally present the 2020 awards to Vanessa Peterson, Sally Birch, and Brianna Ganly, awards that had been postponed due to the 2020 AXAA National Conference cancellation.

Following this, I had the privilege of presenting the 2023 awards. Tony Raftery was presented the Bob Cheary Award for Excellence in XRD for his long career developing the X-ray analytical capabilities at QUT, and similarly developing a generation of new X-ray scientists to use them. Joel O'Dwyer was presented the Keith Norrish Award for Excellence in XRF for developing novel and impactful methodology in online XRF analysis. These awards recognized their exceptional achievements and their dedication to X-ray and neutron science, as well as their significant contributions to AXAA.

Figure 1. The day session featured an ICDD workshop and invited science talks. Shown is Dr Nick Farmer (CSIRO) presenting on the use of autoencoders with XRF map datasets

Figure 2. The 2020 award winners left to right: Brianna Ganly, Sally Birch and Vanessa Peterson, with former AXAA President Nathan Webster.

Frederick Marlton was then awarded the ANSTO Early Career Researcher (ECR) Award for Excellence in Analysis by Mike James, Director of the Australian Synchrotron (ANSTO). These awards are a testament to the outstanding contributions of these individuals and their commitment to our community.

Finally, we also celebrated two new AXAA Life Memberships awarded to Vanessa Peterson and Damian Gore. These honors not only recognize their remarkable research but also their long standing and active involvement within AXAA.

I would like to acknowledge the great support of our event partner ICDD, and additional sponsors Diffraction Technology, CSIRO and ANSTO. Most of all, I was so grateful to see the enthusiasm of AXAA members on the day. The dinner was very well attended and the conversation vibrant and lively such that our time went too quickly and we needed to be nudged out politely by the venue at the end. I take this as a sign that we should do this again!

Figure 3. The 2023 award winners left to right: Tony Raftery, Frederick Marlton and Joel O'Dwyer (far right), with current AXAA President Jessica Hamilton (2nd from right).

Warm regards,
Jessica Hamilton
AXAA President

Event Report - AXAA's Melbourne Networking Day

I am pleased to share with you a recap of the recent Melbourne AXAA Networking Day held on 9th June at the National Centre for Synchrotron Science.

The event featured keynote presentations from Dr. Niloofar Karimian of CSIRO and Dr. Justin Kimpton of ANSTO. Dr. Karimian's presentation delved into the realm of applied X-ray techniques in environmental geochemistry. Her research highlighted the intriguing behavior of antimony and arsenic within iron oxide minerals and their transformations over time, uncovering valuable information about their distinct interactions. Dr. Kimpton's update on the Advanced Diffraction and Scattering (ADS) beamlines under construction at the Australian Synchrotron showcased the exciting possibilities these facilities will offer, along with a glimpse into the progress of their construction.

Our networking morning tea sponsored by **Dectris** offered a wonderful opportunity for attendees to re-connect. Additionally, participants had the chance to gain insights into the functionality of the Australian Synchrotron's beamlines through a facility tour.

One of the highlights of the day was the engaging presentations by three exceptional students. Claudia Giarrusso, a PhD student from Monash University, shared her research journey into the

Figure 4. Participants at the Melbourne AXAA Networking Event on 9 June at the Australian Synchrotron

catalytic potential of silver(I) amido complexes and their unique characteristics, which present new possibilities for catalysis. Maria Paulsen, a PhD student from Monash University, shared X-ray tomographic analysis of long-preserved organisms trapped in amber from Anglesea, Victoria, revealing the secrets of prehistoric life in Australia. Ghazal Baghestani from Swinburne University also shared her work studying the interface between organic and inorganic materials in water oxidation catalysis.

We were honored to award three student prizes for outstanding contributions, with Maria Paulsen securing the first-place prize. Congratulations to all the students for their remarkable work!

In closing, the AXAA event provided a platform for sharing excellent science, new advances, and bringing the Melbourne community back together in person. We extend our gratitude to all participants, sponsors, and speakers for making this event a resounding success.

The State of X-ray Absorption Spectroscopy at the Australian Synchrotron

Valerie Mitchell, Beamline Scientist
Australian Synchrotron, ANSTO

Introduction

X-ray photon absorption and the relaxation processes that follow are studied in X-ray Absorption Spectroscopy (XAS) and can yield valuable information about the oxidation state and local environment of an element of interest. While lab-based XAS instrumentation is increasingly viable, synchrotron radiation remains the best option for rapid acquisition of high quality spectra. In this article we begin by explaining the history and technique in more detail before summarizing existing XAS capabilities at the Australian Synchrotron. We will then introduce two new beamlines which have recently been opened to the user community, MEX 1 and 2.

The History and Theory of XAS

One of the earliest descriptions of the phenomenon of X-ray absorption was published in 1920, when Dr Hugo Fricke collected spectra on a series of elements and noticed distinctive oscillations in the spectra around and above the absorption edge (Figure 1). This ‘complex structure’ was difficult to study with existing X-ray sources and detectors which required prohibitively long data acquisition times and produced low quality data. It wasn’t until the 1950s that the theory underpinning XAS began to emerge, helped along by the construction of the first synchrotrons available for XAS meas-

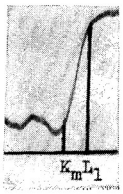

Fig. 1.
Aluminium.

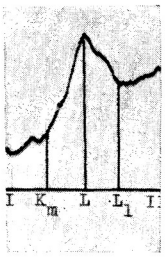

Fig. 2.
Phosphorus.

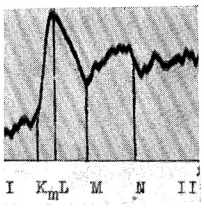

Fig. 3.
Sulphur.

Fig. 4.
Potassium.

Fine Structure of Absorption.—The spectrograms show that the discontinuity has a rather *complex structure*, a result in advance of those obtained by earlier investigators. A *photometric study* of the plates was made in order to obtain a more accurate knowledge of the detailed structure of the absorption limits.

Figure 1. Figure and text from "The K-Characteristic Absorption Frequencies for the Chemical Elements Magnesium to Chromium" ***Hugo Fricke****, 1920*

urements. Even then, the beam in early synchrotrons was too unstable to produce high-quality spectra. It would take another 20 years before synchrotron storage rings could maintain sufficient beam stability for X-ray absorption spectroscopy, allowing XAS to come into its own as a viable analytical technique (Figure 2)

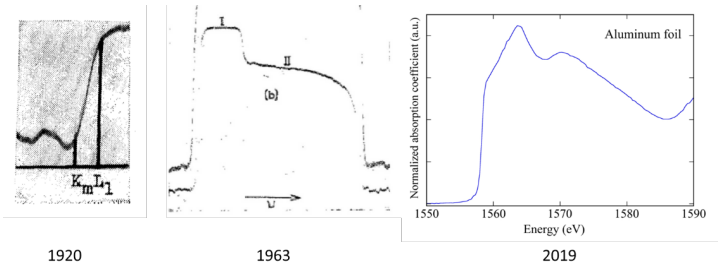

Figure 2. Comparison of XAS spectra of aluminium foil from 1920, 1963 taken at an early synchrotron, and 2019 taken at a modern synchrotron facility

Farrel Lytle, a pioneer of XAS science and developer of the modern theory said after his first trip to one of these new synchrotrons in the 1970's that '*In one trip to the synchrotron we collected more and better data in 3 days than in the previous 10 years. I shut down all three X-ray spectrometers in the Boeing laboratory. A new era had arrived.'*

The advent of storage rings in conjunction with synchrotrons provided a source of X-rays with stable energy and high brilliance, reducing the signal to noise ratio in XAS data by a factor of 10^4, facilitating the development of our current understanding of XAS theory.

In X-ray absorption spectroscopy an element of interest is bombarded with X-rays with sufficient energy to excite inner shell electrons, either ejecting them from the atom entirely or promoting them to a vacant outer shell. Core electrons are bound to the atomic nucleus with a characteristic binding energy, which is unique to each element and varies with the element's chemical environment and oxidation state. Thus by determining the energy required to eject an electron, these material properties can be investigated. The ejected electron can then interact with other atoms in the local environment, and these interactions lead to further changes in the absorption properties of the element as the energy of the X-ray beam is varied. Because of this, information about the neighboring atoms such as interatomic distances, disorder, and coordination number can also be obtained. The energy at which inner shell electrons are ejected is referred to as the 'absorption edge', and the immediate area around the edge is referred to as X-ray Absorption Near Edge Structure (XANES) or Near Edge X-ray Absorption Fine Structure (NEXAFS) while the portion of the spectrum be-

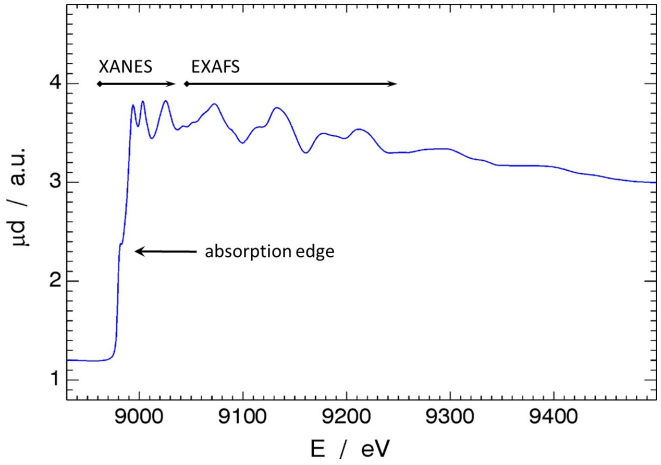

Figure 3. Regions of interest in XAS

yond the edge is called Extended X-ray Absorption Fine Structure (EXAFS) (Figure 3).

The XANES/NEXAFS region provides information about the oxidation state and geometry of the element, while the EXAFS region allows the determination of local environment (e.g. interatomic distances, disorder, coordination number).

The ejection of an inner shell electron results in an atom in an excited state. There are two types of relaxation pathways which the atom can then undergo, depicted in Figure 4. The first is fluorescence, in which an electron in either a M or L shell moves into the vacant K-hole. As the electron moves to a more stable configuration, an X-ray photon equivalent to the energy gap between shells is emitted. These photons produce characteristic emission lines termed K_α and K_β when electrons are transitioning from the L and M shells respectively.

In the second decay pathway, an electron moves from the L shell into the vacant K orbital with release of a K_α photon, but that photon is then reabsorbed by an electron in the M shell, with ejection of the M shell electron. This is called the Auger effect. The relative rates of these two decay processes varies with atomic number, with heavier elements more likely to produce fluorescence and lighter elements more likely to produce Auger electrons.

X-ray absorption spectroscopy monitors either the number of photons absorbed, the number of

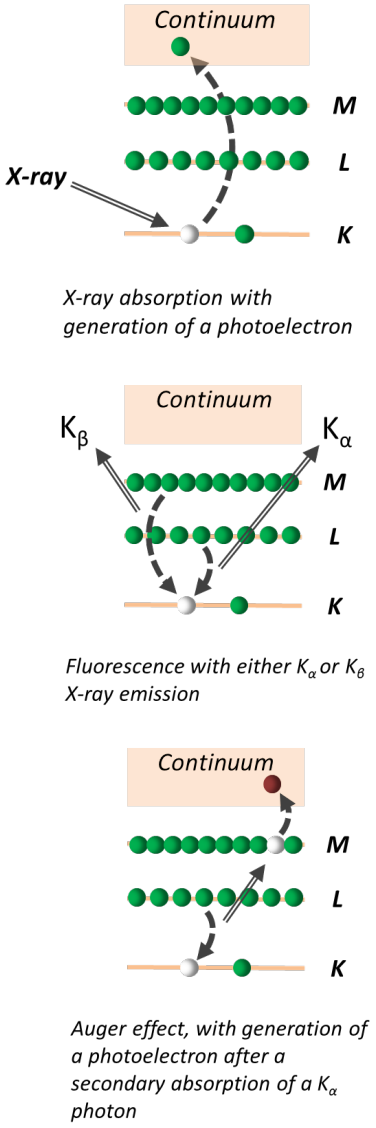

Figure 5. The processes of excitation and relaxation in XAS

fluorescence photons emitted, or the number of electrons ejected as the X-rays are stepped in energy across the absorption edge. A transmission experiment measures the amount of light absorbed directly by comparing the incident beam and the transmitted beam. This is suitable for higher concentration samples that transmit a sufficient amount of X-rays. A fluorescence experiment will monitor the emission of K_α or K_β photons, which will be directly proportional to the number of incoming photons absorbed. Likewise, the emitted photoelectrons can be detected by a suitable analyser. A final detection method called drain current analysis measures the electrons

which are ejected from the sample as a result of X-ray absorption by monitoring the amount of current required to replenish the ejected electrons.

The successful application of each of these techniques varies considerably depending on factors such as the sample, energy range, and beamline configuration, as detailed in the next section.

Current state of XAS at the Australian Synchrotron

XAS beamlines are typically classified according to the energy range of the X-rays that are employed, which dictates which elemental absorption edges are accessible to scientists. This energy range is determined by the characteristics of the X -ray source as well as the optics used to collimate and focus the beam. Hard X-ray beamlines generally have energies above 5 keV while soft X-ray beamlines operate in the 0.1-3 keV range. Medium or tender X-rays span the energy range between the two. The Australian Synchrotron hosts two mature beamlines, the Soft X-ray Spectroscopy Beamline and the X-ray Absorption Spectroscopy Beamline (which is a hard X-ray beamline). It is our pleasure to introduce a new pair of sister beamlines, the Medium Energy X-ray Spectroscopy beamlines, which will complement the existing XAS capabilities and enable exciting new research in Australia. Here we provide an overview of the capabilities, advantages, and limitations of the four systems.

Soft X-ray Spectroscopy (SXR) Beamline

SXR covers an energy range from 90 –2500 eV, which allows researchers to probe the K-shells of elements from beryllium (111 eV) to sulfur (2472 eV) as well as the M- and L- shells of heavier elements. At these lower energies, X-rays are strongly attenuated in air and so the beam path and sample are kept under ultra-high vacuum, which limits the type of samples that can be analysed to non-volatile materials. A further implication of the weakly-penetrating X-rays is that SXR is a surface sensitive technique, only penetrating the top 100 to 200 nm, as opposed to hard X-ray analyses which are typically bulk techniques.

The nature of the SXR beamline dictates the use of different detection methods from those of the hard X-ray regime. One primary distinction is that the UHV environment allows the analysis of electrons ejected from the surface. In the presence of atmospheric gas molecules, fluorescent photons which are massless can escape the sample and reach a detector but photoelectrons, which do have mass, will collide with gas molecules. Furthermore, for lower Z elements the production of Auger electrons dominates the photo-excitation decay processes. Thus on the SXR beamline some of the unique analyses are of photoelectrons, such as X-ray Photoelectron Spectroscopy (XPS) and Angle Resolved Photoelectron Spectroscopy (ARPES).

The SXR beamline at the Australian Synchrotron employs a type of insertion device called an undulator. There are various types of insertion device, which are magnetic components of the synchrotron ring that stimulate increased emission of photons with characteristic intensities and energy distributions. An undulator produces very bright light over a narrow energy range. The result of this is that the SXR beamline is excellent for energy scans across smaller ranges, and focuses on NEXAFS (XANES) analyses which examine the absorption edge, but it is poorly suited for EXAFS which measure an extended energy range.

X-ray Absorption Spectroscopy (XAS) Beamline

The XAS beamline spans an energy range from 5-31 keV, which can access the K-shells of elements from titanium to antimony. Harder X-rays don't require UHV, but attenuation by atmosphere is still an issue at the lower end of the range and thus the flight path is flushed with helium. The XAS beamline cannot measure electron yield, and instead measures the number of photons absorbed by a sample in transmission mode, or the number of fluorescent photons emitted by the sample in fluorescence mode. The XAS beamline employs a

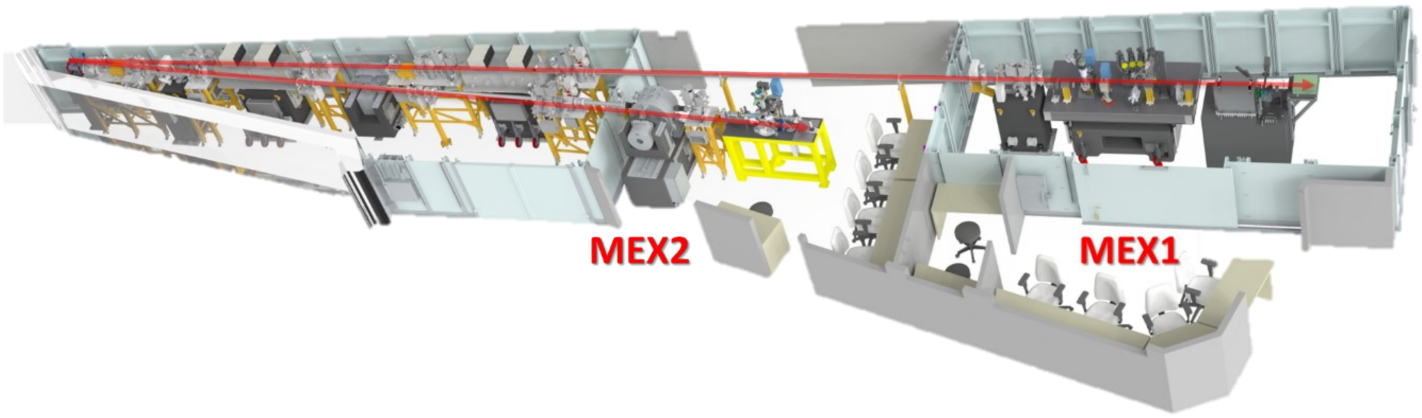

Figure 5. Layout of the MEX1 and MEX2 beamlines.

type of insertion device called a wiggler which, in contrast to the SXR undulator, produces a beam with increased brightness across a larger energy range. With this insertion device, EXAFS analysis is possible, but one drawback is that the flux is so high with a focused beam that sensitive materials eg biological samples often incur significant radiation damage which destroys data quality.

Because XAS does not require rigorous UHV conditions for operation, the sample format varies widely and can include solutions or solids in various *in situ* sample environments. Users often bring their own apparatuses, including electrochemical and battery cells. One exciting new development on the XAS beamline at the Australian Synchrotron is slew scanning, in which the monochromator is continuously scanned across a chosen energy range rather than moved in discrete steps. This dramatically decreases the amount of overhead per energy point, and allows for quite rapid scans, with an EXAFS scan possible in under a minute rather than the 30 minutes previously required. This is of great value in *in situ* measurements.

Medium Energy X-ray Spectroscopy Beamlines

The MEX beamlines were designed to compliment XAS and SXR and address capability gaps. MEX1 and MEX2 share a photon source, which is a bending magnet rather than an undulator or a wiggler. Bending magnets produce lower flux across a wide range of energies, thus enabling EXAFS (in contrast to undulators) and decreasing the risk of radiation damage to sensitive materials (in contrast to wigglers). The desire for MEX was to span the energies from around 1.5 to 13 keV, which covers the gap between the hard and soft X-ray beamlines. The lower end of this range would require that the flight path is under vacuum, while the higher end could be accessed under a helium atmosphere. Rather than attempting to build a single experimental station that achieved this full range, it was decided to split the incoming beam, directing one branch sideways using a horizontal mirror Figure 5. This allows one experimental station to be optimized for the upper energy range (MEX1) and the other to be optimized for the lower energy range (MEX2).

MEX1

MEX1 spans 3.5-13.6 keV for bulk measurements. In this regime helium is used along the flight path. MEX1 is therefore able to reach elements beyond those of XAS, down to the potassium K-edge. MEX1 has a larger defocused beam and lower flux density, and so it is able to measure biologically relevant elements like potassium and calcium in biological samples while minimizing beam damage. As in XAS, MEX1 can accommodate a wide range of sample formats including solids and liquids, and can also be used with user supplied *in situ* environments.

In addition to bulk XAS measurements, MEX1 will host a microprobe endstation for scanning X-ray fluorescence microscopy. This system will employ a microfocused beam adjustable between 2 and 10 µm. With the help of additional harmonic rejection, the microprobe will be able to reach lower energies than the bulk sample environment, with an energy range between 2.1 and 13.6 keV. This will allow the analysis of important biological elements like sulfur which are currently inaccessible at the existing XFM beamline which has an energy range of 4.1-27 keV. Users will be able to analyze samples at ambient temperature under helium or at cryogenic temperatures via a liquid nitrogen cooled cryostream.

MEX2

MEX2 is the lower energy branch of the pair, with an energy range of 1.7—3.5 keV. Similar to SXR, MEX2 can be run under high vacuum and so drain current (which requires photoelectron ejection) can be measured. The sample format is more limited on MEX2, with current sample mounts for fluorescence and drain current measurements are identical to those used on the fast NEXAFS system on SXR. These sample mounts consist of stainless steel rulers which are slotted into a magnetic head containing potentiostat connections. Samples are spread thinly on the ruler or a bit of conductive tape. As in SXR, drain current measurements are very surface sensitive. Transmission measurements are also possible, although due to increased attenuation at these low energies the sample must be extremely thin.

Current and future MEX

Both MEX beamlines are currently accepting merit proposals but are still under development, with further capabilities to be delivered over the next year. These will include High Energy Resolution Detected X-ray Absorption Spectroscopy (HERFD-XAS) on MEX2 and additional sample environments such as liquid helium cooled cryostats as well as a furnace. Users are encouraged to contact the beamline staff regarding experiment feasibility, and to check the MEX user wiki for current capabilities accessible via Medium Energy X-ray Absorption Spectroscopy Beamline (MEX-1 and MEX-2) | ANSTO.

Conclusion

The addition of the MEX beamlines completes the suite of XAS analyses available at the Australian Synchrotron. Prior to MEX, there was an energy gap between SXR and XAS which prohibited EXAFS analysis of significant elements especially sulfur and phosphorous. Users now have access to the XAS measurement in energy range from 90 eV up to 31 keV. Furthermore, the MEX1 microprobe station will allow analysis down to 2.1 keV, extending the existing microscopy capabilities found at the XFM beamline. As discussed in this article, each energy range comes with some benefits and limitations, and it's always recommended to contact the relevant beamline team to discuss your experiment prior to proposal submission. For further information please visit the ANSTO website:

The Australian Synchrotron | ANSTO Research Facilities | ANSTO

Or reach out to the beamline teams:

XAS

as-xas@ansto.gov.au

SXR

as-softxray@ansto.gov.au

MEX

as-mex@ansto.gov.au

AXAA Community News

2023 SPECTRA^{plus} School - Australia

Our SPECTRA^{plus} School Australia is scheduled to take place on 13-17 Nov 2023 at our training facilities in Preston. This hands-on course is an introduction to SPECTRA^{plus} Version 3/4 for WDXRF systems, and will cover alignment, calibration and maintenance. To facilitate interaction between participants and trainers, limited seats are available on a first-come-first-serve basis.

Register and get more information here: https://www.bruker.com/en/services/training/elemental-analyzers/application-trainings/spectraplus-school-au.html

Special plenary session at the Science Summit around the 78th United Nations General Assembly (UNGA78)

Our sessions will examine how equitable access to big science institutions can accelerate the progress of the UN's sustainable goals. In particular, a focus on how the global science community could contribute to building research capacity, diverse expertise, and innovative funding solutions to the Caribbean and African synchrotron facilities.

When: Thursday September 28, 2023 9:00am - 12:30pm EDT (NEW YORK TIME)

ONLINE – register here: Science Summit at United Nations General Assembly (UNGA78)

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AXAA Membership

All registered participants of the AXAA-2017 conference are automatically granted AXAA membership for 3 years. Alternatively, new memberships can be obtained free of charge, by making an application to the National Council.

Candidates should send the membership form from the AXAA website, and a short statement about how they intend to contribute to the organisation, to the National Council Secretary Anita D'Angelo.

AXAA Resource Centre

There are a range of resources available on the AXAA website, including video recordings of the two Public Lectures at AXAA-2017, tips for Rietveld Analysis, Clay Analysis, XRF tips, and more. We welcome further contributions to our Resource Centre.

Next AXAA Newsletter

The next issue of the AXAA Newsletter will be distributed in December 2023. Please feel free to send contributions for the newsletter to Valerie Mitchell at *ausxray@gmail.com*. Any comments or feedback about the Newsletter are welcome.

A Day in the Life of an X-ray / Neutron Scientist

We are seeking posts for our 'Day in the Life' series. If you'd like to contribute, or know someone who might be interested, please contact National Council