Beamline 5: X-ray absorption spectroscopy

05

Potential Research Fields

Life sciences

- Biological research and drug design
- Biotechnology and bio-sensors
- Plants and crops

Physical sciences

- Sustainable environment
- Forensics
- Advanced materials
  - Ceramics
  - Micro-electronic and magnetic materials
  - Biomaterials
- Mineral exploration and beneficiation
- Earth sciences
- Oil and gas production and distribution
- Agricultural technology
- Chemical reactions and catalysts

Advanced manufacturing

- Production of micro-devices

Introduction

X-ray absorption spectroscopy (XAS) is a well-established, quantitative analytical technique used by both academia and industry to obtain atomic-scale structural and chemical state information for a wide range of systems in both liquid and solid form. XAS probes both the short- and medium-range order of a sample and as such is complementary to x-ray diffraction.

An XAS spectrum is typically separated into XAFS (extended x-ray absorption fine structure) and XANES (x-ray absorption near edge structure) regions. Analysis of XAFS yields structural information such as bond length, coordination numbers and disorder. In closer proximity to the absorption edge, analysis of the XANES yields chemical information such as the local coordination geometry and oxidation state of the absorbing atom.

XAS is a sufficiently well established and broadly used technique for it to be commonly offered as a commercial analytical service by both synchrotron facilities and private companies.

Advantages of a Synchrotron Source

An XAS experiment is the measurement of the absorption coefficient of a sample as a function of incident photon energy. In multi-elemental samples, this commonly necessitates the careful examination of multiple absorption edges and thus XAS measurements are not practical on a laboratory-based system.

XAS measurements need an intense, tunable source of photons afforded only by a synchrotron. XAS beamlines are thus available at synchrotrons worldwide and are used by scientists from the biological, biochemical, chemical, earth, environmental, materials and physical sciences and engineering. The maturity of the technique in experimental performance and data analysis is such that non-specialists now comprise a significant fraction of the user base.

Synchrotron facilities with an energy range comparable to the Australian Synchrotron typically have multiple beamlines dedicated to this technique. For example, at the Photon Factory, Japan, XAS measurements comprised 23% of all experiments over all beamlines performed in 2001.

User Community

The Australian XAS user base currently exceeds 70 practitioners with an anticipated increase to 150 when a domestic facility is operational. XAS users comprise the largest fraction of the Australian synchrotron science community and XAS experiments comprise the largest fraction of Australian synchrotron science measurements. At present, Australian access to XAS capabilities is facilitated by the ASRP at the Australian National Beamline Facility (ANBF) at the Photon Factory, Japan. At this single multi-purpose beamline, XAS measurements represented 42% (70.5 days) of all experiments performed in 2001. Flux limitations from the bending-magnet source at the ANBF inhibit XAS experiments on dilute samples. For such measurements, Australian XAS users seek access to alternative synchrotron facilities worldwide. In 2001, this accounted for an additional 50 days of XAS experiments performed by Australian scientists. Total Australian XAS usage in 2001 was ~120 days/year with an estimated demand of ~180 days/year. Demand for XAS measurements in 2001 was thus sufficient to utilise all available time on a dedicated wiggler-based beamline at any synchrotron facility worldwide.

Research Applications

Historically, Australian XAS research has been characterised by both diversity and excellence. The former is demonstrated by the breadth of disciplines represented in the user community, while the latter is apparent from the level of ARC funding accorded synchrotron-based research proposals.

A dedicated XAS beamline at the Australian Synchrotron will further these traits. Research applications are widespread and some examples are discussed below.

Biological sciences

Therapeutic target site identification: metal (Cu, Zn and Fe) binding to amyloid ß-peptide, the latter found in all biological fluids, may be responsible for some of the pathological effects of Alzheimer's Disease. A determination of the metal-binding site yields a potential therapeutic target site. This specific example demonstrates the complementary nature of biological XAS and protein crystallography and the common necessity of using both techniques for a structural solution.

Biochemical sciences

Carcinogens: to characterise the structures of a range of reactive Cr complexes with biological reductants. This research will provide important new insights into metal-based toxicology.

Anti-cancer technologies: investigations of cobalt (Co) and platinum (Pt) anti-cancer drugs with the aim of developing new technologies that enable the determination of the oxidation state in situ in different regions of tumours and in models of hypoxic tumours.

Anti-inflammatory drugs: characterisation of new drugs in the solid state, and in solution, pharmaceutical formulations and biological fluids. This research has been essential in determining the stability of the drugs in pharmaceutical preparations and in understanding the pharmacology.

Chemical sciences

Transition metal complexes: elucidation of the molecular details of the chemistry associated with enzyme catalysis. This research aims to understand the influence of redox or charge state on the electronic and molecular structure of metal complexes or clusters in order to anticipate (and ultimately control) the reactions and reactivity of transition metal catalysts.

Earth sciences

Ore metals: identification of the metal complexes involved in the transport of ore-metals (Cu, Au, Ag) by supercritical hydrothermal solutions to form economically important ore deposits. Interest is focussed on the partitioning of Cu between coexisting brine and vapour phases during boiling, as this process may explain the relationship between different ore types in a common geological setting. An improved understanding of the formation of these major economic deposits may aid in predictive exploration.

Magma oxidation: determination of the oxidation state of elements in magmas (silicate melts). The abundance of elements in the mantle relative to those in meteorites that are thought to have condensed from the primitive solar nebula can be used to help constrain models for the differentiation and evolution of the Earth. Australian scientists have recently used XAS measurements performed at high temperature to show that approximately half the chromium (Cr) in a mid-ocean ridge basalt (the most common rock on the surface of the Earth) at 1400°C is Cr^{2+} even though this oxidation state has never been identified in a terrestrial material.

Environmental sciences

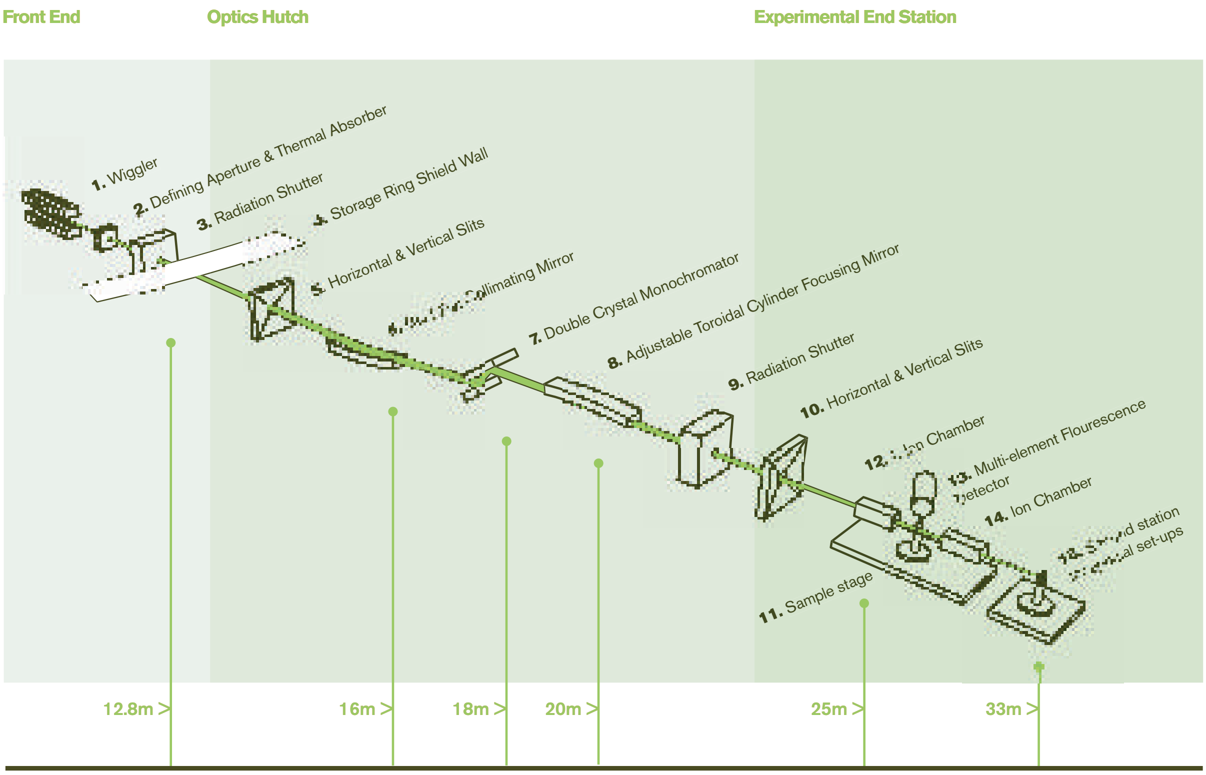
Radionuclides in the marine environment: investigating the solid state redox speciation of metals in particles suspended in marine water. Redox speciation changes of Fe and Mn play an important role in the formation and growth of natural particles and the sorption and release of radionuclides and trace elements in the marine environment. Using XANES to define the extent and dynamics of these redox changes is important to elucidate basic mechanisms and establish sorption and transport models.

Materials sciences

Semiconductor device fabrication: characterisation of ion-implantation-induced disorder in semiconductor substrates with application to both electronic and photonic device fabrication. The ion implantation process is one of several basic building blocks used in the production of all modern semiconductor devices and the form and extent of residual ion-implantation-induced disorder ultimately governs device performance. These studies are of a fundamental nature with both scientific importance and technological relevance.

New science

Nanoscience: XAS is an ideal technique to yield insight into the novel properties exhibited by materials at the nanometre scale. XAS studies have been initiated by Australian scientists to study both semiconducting and metallic nanoparticles in a variety of matrices for application to photonic devices and chemical catalysis, respectively.



BEAMLINE 5 X-ray Absorption Spectroscopy

Figure BL5.1. *Schematic of the x-ray absorption spectroscopy beamline*

Ultra-dilute measurements: New developments in photon production and detection incorporated in the XAS beamline will make measurements at the ultra-dilute level possible. This will enable pioneering experiments in a variety of fields including biochemistry and engineering.

Fast-scanning/time-resolved measurements: fast-scanning XAS will be used to develop methodologies for determining the structures of intermediates in enzymatic processes using standard stopped-flow and other mixing technologies. This will provide new insights into biochemically important pathways that were not assessable previously.

Electron-beam ion trap: a new and novel device that can be coupled to the XAS beamline and enable a new generation of fundamental experiments to reduce uncertainties on tests of quantum electrodynamics in the x-ray regime by an order of magnitude. Though a similar proposal is under consideration at an American facility, this represents another opportunity for Australian scientists to be world leaders.

Beamline Design

Because of the current usage and demand, a dedicated wiggler-based XAS beamline is proposed for the Australian Synchrotron. The combination of wiggler, collimating mirror, double-crystal monochromator and focussing mirror is recommended by the Australian XAS community and international experts.

It will be a user-friendly beamline appropriate for both novices and seasoned practitioners.

Table BL5.1 Beamline operating modes

Energy	Operating Mode
<~ 10 keV	The wiggler will operate at K = 10 and will yield excellent harmonic rejection to < 5 keV.
>10 to ~20 keV	The combination of the wiggler spectrum for K = 20 will provide good intensity in the 10–20 keV range and very good harmonic rejection at 30–60 keV.
>20 to ~35 keV	The wiggler will operate at K = 20 or higher, depending on the photon energy required. A higher index set of monochromator crystals will be utilised.
>35 keV	Higher photon energies will exceed the critical energies of the mirrors so the beamline must be able to operate with both mirrors withdrawn.

Notes: The combination of mirrors, mirror coatings and a variable-field wiggler enables the precise optimisation of the beamline for a given experiment. Four modes of operation are envisioned. K is the undulator factor and defines the opening angle of the of insertion device.

Sample size and type will be varied and include both solid and liquid samples. Measurement capability at temperatures from ~10–1273 K (e.g. a cryostat and furnace) will be necessary.

Detectors including ion chambers, Stern-Heald-Lytle detectors and a multi-element solid-state detector are necessary. Recent innovative designs including log spiral and pixel array detectors also warrant consideration.

Two hutches in tandem – the first to house the standard XAS measurement station and a second to accommodate experiments that necessitate prolonged set-up time (for example, an ultra-high vacuum deposition chamber) are required.

A wiggler source is necessary to achieve the desired combination of energy and flux. The flux from a 2 T, 16 cm period advanced variable-field, multi-pole wiggler not only satisfies the needs of the Australian XAS community but provides the flexibility to optimise the beamline for specific experimental requirements of energy range, energy resolution, flux and harmonic content.

Improved energy resolution will be achieved with a collimating mirror (a bent flat).

A fixed-exit-height, double-crystal monochromator able to withstand the full power output of the wiggler is required. The first crystal will therefore have in excess of 2 kW of power impinging upon it. The capability of exchanging crystals must be rapid and multiple crystal sets will be needed to cover the energy range of the beamline.

Beamline 5 – X-ray Absorption Spectroscopy	
Source	Wiggler (3 T)
Energy range	4–30 keV, with option for up to 65 keV
Resolution $\Delta E/E$	$<10^{-4}$
Beam size at sample (horizontal × vertical)	~0.2 × 1 mm
Photon flux	$>10^{12}$ photons/sec at sample