ACCELERATOR MICROANALYSIS

Claudio Tuniz
Australian Nuclear Science and Technology Organisation
Menai, 2234 NSW Australia

Abstract

The Australian Nuclear Science and Technology Organisation (ANSTO) is involved in advanced research programs based on the use of nuclear science and technology for materials microanalysis. This paper is a review of accelerator-based probes to characterise environmental, biological and industrial materials. Most examples are inspired by the ANSTO research program.

1. Introduction

Particle accelerators have been developed more than sixty years ago to investigate the nuclear and atomic structure. A major shift toward the use of accelerators in the analysis of materials composition and structure for scientific and industrial applications has been witnessed in the last two decades. Tandem Van de Graaff accelerators have evolved into specialised tools for ion beam analysis (IBA) and accelerator mass spectrometry (AMS). Synchrotron accelerators have become dedicated facilities, optimised for emission of bright electromagnetic radiation, an ideal microanalytical probe for biology, materials science and other disciplines. Finally, high-energy proton accelerators are used in spallation sources for producing pulsed beams of neutrons to characterise the structure of matter in condensed states.

2. Ion accelerators

Ion accelerators used for analysis of materials are, for the most part, either single-ended or tandem type Van de Graaff accelerators. Very often these are machines which were originally constructed for nuclear physics research and have been turned to other uses as the effort in low-energy nuclear physics faded away. On the other hand, the field has grown to such an extent that machines designed specifically for analytical applications now exist.

Two ion accelerators are available at the Lucas Heights Science and Technology Centre, a 3 MV single-ended Van de Graaff accelerator and an 8 MV Tandem Van de Graaff accelerator.

In the 3 MV Van de Graaff accelerator, positive ions are produced from neutral gasses such as hydrogen and helium. The choice of ion type and its energy depends on the elements of interest in the material being analysed. This accelerator was installed in 1963 to produce neutron beams with characteristics suitable to study materials of interest in reactor design. The original research program was related to studies of neutron-induced reactions and fission. In the last 20 years, research programs related to ion beam applications in science and industry became dominant.

The ANTARES tandem accelerator is based on the FN tandem accelerator originally built by High Voltage Engineering for Rutgers University (New Jersey, USA). Since its arrival in Australia, in 1989, the accelerator has undergone a complete refurbishment and upgrade. Major items in this transformation are: use of SF_6 insulating gas, new spirally-inclined accelerator tubes, Pelletron charging system, 60-sample computerised ion-source, high resolution and high rigidity injection magnet and fast sequential isotope injection [Tuniz, 1997a]. Versatility is allowed by multiple beamlines for ion beam analysis and accelerator mass spectrometry.

3. Ion Beam Analysis

Ion accelerators provide a variety of MeV-energy ion beams. Advanced methods for production and focusing of ion beams have been developed over the last decades. Ion beams lose energy by

ionization of the atoms composing the stopping material caused by the interaction of the Coulomb field of the projectile with the atomic electrons and also by nuclear scattering from the nuclei of the atoms. The range of ion beams in materials is short, with a relatively well defined end point. By comparison, x-ray beams are attenuated according to an exponential law and sample a much greater amount of material.

Ion beams are used for trace element determinations using the characteristic x rays produced in the ionization process. Ion beams can also interact directly with atomic nuclei. Nuclear reactions, including elastic and inelastic scattering or Coulomb excitation, are useful to identify specific elements and nuclides present in the sample. Concentration of individual elements or isotopes as a function of depth is possible using narrow nuclear resonances and energy loss of ions as they travel in the material.

Detection methods for x rays, γ rays, charged particles and neutrons have been developed in parallel with the development of accelerators, ion sources and other instruments necessary for the production of ion beams. This work has been driven by the need for basic understanding of nuclear physics, by practical considerations related to nuclear power, medical applications, etc. Many of the analytical uses of ion beams have also stemmed from the applicability of these methods to study semiconductor materials used for production of various types of electronic devices.

Combination of different ion beam analysis techniques such as particle induced x-ray emission, nuclear reaction analysis, activation analysis and elastic recoil detection can be used to determine elemental compositions for elements from hydrogen to the transuranic elements.

3.1 Proton induced X-ray emission (PIXE)

PIXE is by far the most widely applied of all ion-beam related techniques used in analysis of environmentally related materials. PIXE is used for the routine detection of elements with atomic numbers greater than perhaps 13 using simple energy-dispersive x-ray detectors. The detection limits are not constant across the periodic table, but are extremely good in many critical regions such as for the transition elements and for heavy elements such as lead and mercury. It can be used in different modes: broad beam for analysis of bulk samples and microbeam for measurement of individual features. Maps of the composition of heterogeneous samples can be obtained by rastering the beam across the sample and making a point-by-point determination of the elements present.

3.2 Nuclear reaction analysis (NRA)

Nuclear reactions are used to make sensitive determinations of many specific isotopes. In general, nuclear reactions and elastic scattering are used for detection of specific elements/isotopes throughout the periodic table. However, nuclear reaction analysis is particularly helpful for elements with $Z < 20$ since the sensitivity of PIXE decreases rapidly for smaller atomic numbers. Strongly resonant nuclear reactions induced by ^{15}N and ^{19}F beams are used to probe the concentration of hydrogen as a function of depth. Inelastic scattering of protons (PIGE - proton induced gamma-ray emission) is used to detect Li, B, F, Na, Mg and Al. (d,p) reactions can determine the concentration of oxygen and carbon.

3.3 Elastic Recoil Detection (ERD)

When incident ions interact elastically with target atoms, the target atoms are knocked forward. By measuring the energy of the knocked-on atoms, information on their concentration and depth can be obtained.

The ERD system on the ANSTO tandem accelerator uses 77-MeV iodine beams to measure depth profiles for a variety of elements. Measurements of time of flight and energy provide unambiguously elemental depth profiles. This analytical system has been used by ANSTO groups in studies related to high temperature superconductors and other projects based on surface characterisation.

3.4 Ion microprobes

Ion microbeam analysis uses an ion beam focussed to μm dimensions to image material samples. The imaging can be performed by using secondary radiation induced by the primary ion beam, such as x-rays and nuclear reaction products, or by using the energy loss of transmitted primary ions. Pioneering studies with proton microbeams (50 μm diameter) were performed in the mid sixties at the Lucas Heights 3-MV accelerator [Mak, 1966]. These first experiments paved the way for the modern nuclear microprobes, characterised my sub-micron lateral resolution [Breese, 1996].

A heavy-ion microprobe is presently being developed at ANTARES, the ANSTO tandem accelerator, for surface imaging and depth profiling. This nuclear microprobe is designed to focus a variety of ion beams, including iodine, to lateral dimensions of less than 10 μm.

3.5 Case studies

Aerosols
There is strong international interest in the environmental monitoring of fine particles in the atmosphere. This interest stems from the possible effects of fine particles on health and on global climate change. Recent studies suggest that 50,000 deaths a year are caused in USA by fine particle pollution. These studies are concerned with fine particles of 10 μm diameter or less. The source of these particles are combustion processes from automobiles, fossil fuel burning and industrial processes. ANSTO is involved since 10 years ago in studies on the impact of atmospheric fine particles in Australia [Cohen, 1996]. Different IBA techniques are applied simultaneously to thousands of samples to determine the elemental composition of atmospheric aerosols, viz. PIXE (for elements from Si to U), PIGE (for Li, B, F, Na, Mg and Al), PESA - Proton Elastic Scattering Analysis - for H, C and N analysis and RBS (all elements except H). All elements can be determined with sensitivities from 50 pg/m^3 to 50 ng/m^3.

Synroc
Synroc has a high leach resistance in aqueous media. It is difficult to use H_2O to measure the hydrogen incorporated in Synroc, also for the ubiquitous presence of hydrogenous surface contamination. The use of D_2O provides a more sensitive and reliable method for this kind of studies. ERD techniques have been used at ANSTO to study deuterium depth penetrations and concentrations in Synroc samples to evaluate the chemical reactions taking place during the dissolution of this material at different temperatures [Dytlewski, 1996].

4. Accelerator Mass Spectrometry

AMS incorporates an ion accelerator and its beam transport system as elements of an ultra-sensitive mass and charge spectrometer [Tuniz, 1998]. Multiple selection stages for energy, momentum, velocity and atomic charge plus final identification of nuclear mass and charge with an ion detector makes possible measurements of isotopic ratios some four or five orders of magnitude smaller than is possible with conventional mass spectrometry (MS). The high isotopic selectivity of AMS enables a dramatic reduction of the backgrounds that plague MS: molecular and isobaric interferences and tails of abundant neighbouring masses. For instance, AMS allows an isotopic sensitivity of less than one part in 10^{15} for ^{14}C, ^{10}Be and other radionuclides occurring in nature at ultra-trace levels. The sensitivity of AMS is unaffected by the half-life of the isotope being measured, since the atoms, not the radiations that result from their decay, are counted directly. Hence, the efficiency in the detection of the aforementioned radionuclides improves by several orders of magnitude, depending on the half-life of the radionuclide being measured. The size of the sample required for the analysis is reduced accordingly. Also some stable isotopes, often present in the environment at very low concentrations, such as the rare earth elements (REE) and the platinum group elements (PGE), can be detected by AMS with better sensitivities than low-energy MS.

In the last 15 years, AMS systems have been developed at more than 40 laboratories for the detection of low-abundance radionuclides in environmental, archaeological, biomedical and industrial samples. Electrostatic tandem accelerators are the optimum choice for a variety of AMS applications. Small tandems (1.7 - 3 MV) have been specifically designed for ^{14}C analysis. These relatively low-energy

tandems can also be used to detect other long-lived radionuclides, such as ^{10}Be, ^{26}Al and ^{129}I or stable isotopes. Larger tandem accelerators, originally used for nuclear physics research, can be upgraded and used to analyse a variety of rare radionuclides.

Other accelerators, such as cyclotrons, have been also used in AMS. Cyclotrons allow the achievement of high ion energies by repeated application of relatively low electrostatic fields. However, the principle of cyclotron operation applies only to a specific ion mass so that it can be used to reject unwanted masses with high resolution. Cyclotrons were used for early AMS measurements of some long-lived cosmogenic radionuclides such as ^{10}Be and ^{26}Al. A mini cyclotron has been used to detect ^{14}C at natural abundances, but the practical use of this system will require further developments to allow precise measurements of isotopic ratios.

4.1 AMS with tandem accelerators

In AMS, the element of interest is chemically separated from the original sample and loaded as a target in the sputter ion source of the tandem accelerator.

Negative ions are produced in the ion source and, after a pre-acceleration stage, their mass is analysed by a magnetic field. Following injection into the accelerator, negative ions are attracted by the positive voltage at the terminal and thereby accelerated to high energies (a few MeV), at which point they pass through a gas or a foil stripper located at the terminal and stripped of some of their electrons. Multi-charged positive ions are then further accelerated by the same positive voltage on the terminal. Following the acceleration, combinations of magnetic and electric fields select momentum, energy and velocity of the ions. High-resolution Wien filters, electrostatic analysers, and double focussing magnets provide the selectivity necessary to separate the radionuclide of interest. Finally, the identification of the rare isotope, accelerated at energies of 10-100 MeV, is performed in the ion detector. Depending on the isotopes to be counted, a variety of detectors are available for this final stage of the AMS spectrometer such as ionisation chambers and time-of-flight detectors. Energy, stopping power, range and velocity can be measured to identify the isotopes of interest.

The main advantages of tandems for AMS are firstly, the use of sputter sources producing negative ions and secondly, terminal stripping. The first feature is important as most elements form negative ions and many radionuclides can be analysed. In addition, there are some favourable cases where the interfering isobar does <u>not</u> produce negative ions, e.g. ^{14}N in the analysis of ^{14}C and ^{26}Mg in the detection of ^{26}Al. The stripping of 3 or more electrons at the terminal of the tandem is a powerful stage to reject molecular interferences which are the main limitation for conventional MS.

High precision AMS analysis is carried out by either using simultaneous injection or rapid sequential injection of the isotopes of interest, in order to overcome variability in source output and accelerator transmission. Simultaneous injection restricts the range of masses analysed and has been recently adopted in commercial accelerators dedicated to radiocarbon analysis. Sequential injection allows the development of a more universal system, suitable for the high precision analysis of a wide range of isotopes.

4.2 Long-lived radionuclides

Radionuclides are used as tracers and chronometers in many disciplines: geology, archaeology, astrophysics, biomedicine and materials science. Low-level decay counting techniques have been developed in the last half century to detect the concentration of cosmogenic, radiogenic and anthropogenic radionuclides in a variety of specimens. The radioactivity measurement for long-lived cosmogenic radionuclides, such as ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, is made difficult by low counting rates and in some cases the need for complicated radiochemistry procedures and efficient detectors of soft beta particles and low energy x rays . AMS can measure cosmogenic radionuclides in geological samples up to 10^6 times smaller then those required for conventional techniques, allowing novel applications in geology and environmental science.

An Accelerator Mass Spectrometry (AMS) system has been developed at ANSTO for the detection of carbon-14, iodine-129 and other long-lived radioisotopes. This AMS spectrometer is a key instrument

for scientific projects involving global climate change studies and international nuclear safeguards. Another Australian facility, the AMS spectrometer at the Australian National University, is being used to measure plutonium and neptunium isotopes for environmental and biomedical applications [Fifield, 1997].

4.3 AMS microprobes

Secondary Ion Mass Spectrometry (SIMS) is used for isotopic analysis with high sensitivity and micron-size space resolution. It makes use of a sputter ion source and a mass spectrometer for analysis and detection of the KeV secondary particles (positive, negative or neutral) produced. The use in a SIMS system of an AMS spectrometer improves the detection limit for many elements by several orders of magnitude. This technique is sometimes referred to as super-SIMS.

The first studies with super-SIMS systems showed that limitations arise from contamination by impurities in the Cs sputtering beam and from materials used in the construction of the ion source. Special designs have therefore been developed using magnetic analysis of the sputtering beam and construction of the source from high purity silicon. The super-SIMS system developed at the University of North Texas and Texas Instruments, allows bulk sensitivities of 10^{13} atoms/cm^3 for several elements in the periodic table and may be used for both bulk and depth profiling measurements.

The AMS requirements in super-SIMS do not require high acceleration energy and 2 to 3 MV tandems can be used for the determination of trace elements in geological samples.

A super-SIMS facility, AUSTRALIS, dedicated to the in-situ microanalysis of geological samples, is being developed at the CSIRO in Sydney [Sie, 1997]. This system will be used to measure the fractionation of PGE and REE in petrogenic studies. Other applications are related to detect precious metal distributions in ore minerals.

4.4 Case studies

Global Climate Change

Ice cores are providing the best source of preserved air from which to reconstruct levels of greenhouse gases over recent centuries to millennia. Ice cores from Law Dome, East Antarctica, characterised by high accumulation rates but minimal summer melting, provide an unparalleled time resolution through the Holocene and possibly beyond. In addition, air extracted from the firn permits direct comparison of entrapped trace gas concentrations with modern records. One of the problems is that recent CO_2 growth rate variations are difficult to interpret due to the smearing of ice-core signals induced by the diffusion of air in the firn. In collaboration with the CSIRO Division of Atmospheric Research, we recently succeeded in using the ^{14}C "bomb spike" to determine the age spread and age of CO_2 in Antarctic ice and firn [Levchenko, 1996].

Nuclear Safeguards

Nuclear activities such as reactor operation, fuel reprocessing and uranium enrichment introduce into the environment long-lived radionuclides such as ^{129}I and ^{36}Cl. Accelerator mass spectrometry (AMS) is the analytical technique of choice for the practical analysis of these radionuclides in natural specimens. Isotopic concentrations of 10^6 atoms per gram and isotopic ratios of 1 part in 10^{15} can be detected in very small samples taken from a variety of environmental materials such as water, air, soil and biota [Tuniz, 1997b]. In collaboration with the IAEA and with the support of the Australian Safeguards Office, the ANSTO AMS group has recently analysed ^{129}I in waters and sediments collected by IAEA inspectors at various locations from a nuclear reprocessing plant.

Biomedicine

AMS provides a method for analysing long-lived isotopes of elements for which metabolic and toxicological information is not available. Aluminium, for example, is now considered to be a toxic element, whose accumulation has been identified as the cause of diseased states in chronic renal failure patients. Although still a highly controversial issue, Al has also been implicated in the aetiology of Alzheimer's disease. Yet, aluminium compounds have been used since last century in

water treatment. Without an appropriate radioisotope and being a monoisotopic element, conventional studies of aluminium metabolism have been restricted to large dose quantities of stable Al and as such do not reflect normal physiology. Detection via AMS of the long-lived radioisotope ^{26}Al administered at ultra-trace levels and thus with negligible radiation damage can provide a new avenue to understand the role aluminium plays in biological systems. In a collaborative project, the ANSTO AMS group detected the presence of ^{26}Al in the brain tissue of Wistar rats gavaged with drinking water containing 70 becquerel doses of ^{26}Al [Walton, 1995].

5. Synchrotron radiation

ANSTO manages the Australian Synchrotron Radiation Program (ASRP) which provides Australian researchers with access to synchrotron radiation facilities at overseas synchrotron light sources. These are the Australian National Beamline Facility (ANBF) at the Photon Factory, Tsukuba, Japan, and the Advanced Photon Source (APS) at the Argonne National Laboratory in Chicago, USA.

The Photon Factory is a 2.5 GeV second generation synchrotron light source. The ANBF is installed on a bending magnet port and uses monochromatic synchrotron X-rays in the energy range 4.5-20 KeV. The main instrument is a diffractometer with a detector based on image plates.

The APS is a 7 GeV third generation synchrotron light source, characterized by X-ray beams a thousand of times brighter than the Photon Factory. The ASRP has joined two Collaborative Access Teams (CAT), the Synchrotron Radiation Instrumentation (SRI) CAT and the Consortium for Advanced Radiation Sources (CARS) CAT.

The aim of the SRI-CAT is to develop and implement strategic SR instrumentation based on the use of sub-micron spot size beams, time-resolved spectroscopy, high energy X-ray beams (up to 200 KeV), etc.

CARS are organised along specific disciplinary lines. Australia, via the ASRP, is a member CARS, with guaranteed access to the BioCARS and ChemCars beamline facilities. BioCARS promotes the understanding of basic biological processes providing facilities for X-ray crystallography. ChemMatCARS will support condensed matter studies based on small and ultra-small x-ray scattering and time resolved crystallography.

5.1 XRF microscopy

X-ray fluorescence (XRF) spectroscopy is one of the oldest analytical tools based on x-rays. Synchrotron radiation (SR) has unique properties, very desirable in high-sensitivity elemental analysis using XRF:

- high brightness
- wide energy spectrum
- high degree of polarisation

In general, instruments utilising XRF to obtain two-dimensional maps of element distribution with microscopic resolution are called x-ray microscopes (XRM). The primary requirement for an XRM is a micron-size beam of SR characterised by a high intensity flux.

Focusing of energetic photons is difficult because of the short absorption depth and the refraction index being less than unity. The focusing itself is based on refractors that have bent shapes and usually result in more or less monochromatic beams [Zontone, 1991].

Scientists from the Free University of Amsterdam constructed a focusing device at Daresbury (SERC) with bent silicon crystals, which can increase the photon flux more than 10^4-fold. A double elliptical mirror (Kirkpatrick-Baez) geometry was designed by the Lawrence Berkeley Laboratory that uses parallel beams of photons to produce an image that is demagnified by about a factor of 100 to produce final images of a few micrometers. The mirrors used are multilayers of tungsten carbide

that give a quasi-monochromatic beam in the sample plane. Most recent developments are Fresnel zone plates and tapered glass capillaries. A photon flux of 10^{10} photons per sec and per μm^2 and a minimum detection limit below 10^{-15} g have been obtained at ESRF using a conical glass capillary. This system has been recently used to produce elemental images of fly-ash particles.

6. Neutron beam analysis

The following properties make thermal neutrons very valuable micro-analytical probes:

- deep penetration in materials, useful for in situ studies in furnaces and pressure vessels, in industrially relevant conditions;
- scattering properties suitable for providing contrast between hydrogen and deuterium, a widely used technique to study biological materials, polymers, colloids etc.;
- wavelengths comparable with spacing between atoms, so that neutron scattering provides unique information on atomic structure.
- the magnetic moment of the neutron makes it a unique probe to study magnetic structures.

The traditional means of producing neutrons is by fission in a nuclear reactor. The neutrons produced from such sources are thermalised in a moderator and their wavelength is selected by Bragg scattering from crystal monochromators. Several neutron scattering instruments are available at HIFAR, the ANSTO reactor. In the last few years, ANSTO has coordinated access for Australian researchers to the neutrons produced by ISIS, the spallation source at the Rutherford Laboratory in United Kingdom. ISIS produces neutrons by bombarding a heavy metal target (uranium or tantalum) with a pulsed beam of protons (2.5 10^{13} protons per pulse) accelerated to 800 MeV. Some 25 neutrons are produced for each proton hitting the target. These neutrons are then slowed down in the moderator (water, liquid methane or liquid hydrogen) and used in a variety of techniques such as small-angle scattering, powder diffraction, reflectometry and radiography. The research program spans a variety of scientific applications in biology, condensed matter physics, polymers, surfaces, advanced materials and metallurgy.

7. Conclusions

Determining structure and composition of materials is a fundamental requirement in research and industry. Ions, photons and neutrons produced by particle accelerators offer an array of probes and microscopes, which can provide effectively this information.

8. References

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