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Accelerator mass spectrometry: ultra-sensitive analysis for global science

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Abstract

Accelerator mass spectrometry (AMS) is the analytical technique of choice for the detection of long-lived radionuclides that cannot be practically analysed with decay counting or conventional mass spectrometry. AMS has been used for the analysis of ^{14}C, ^{10}Be, ^{36}Cl and other cosmogenic radionuclides in archaeology, geology and environmental science. In addition, the ultrasensitivity of AMS is being applied in biomedicine to study the exposure of human tissues to chemicals and biomolecules at attomole levels. AMS is also being considered for the detection of anthropogenic radionuclides, such as ^{129}I and ^{236}U, in environmental samples for the verification of the nuclear non-proliferation agreements. The state of the art of AMS is reviewed with examples from some recent applications.

Keywords: AMS; Radionuclides; Environment; Safeguards

1. Introduction

Twenty-four years ago, groups of physicists from the United States and Canada operated an ion accelerator as a high-energy mass spectrometer, achieving unprecedented levels of sensitivity in the measurement of isotopic abundances. This analytical method, called accelerator mass spectrometry (AMS), was first applied to the detection of ^{14}C in natural organic specimens.

Since then, AMS has been applied to other long-lived radionuclides with a profound impact on many branches of science and technology and the range of applications continues to grow. The ultrasensitive detection and accurate measurement of radionuclides in natural specimens at previously unrealised low levels of concentration have enormous implications for studies related to the history of the terrestrial environment. AMS permits measurements of long-lived chronometers and tracers (see Table 1) in samples that may be several orders of magnitude smaller than possible with conventional techniques. The concentration of these radionuclides in natural archives, such as sediments, ice cores and tree rings, provides a precise time frame for environmental change and human development.

More recently, AMS applications also expanded to biomedicine, radiopharmaceutical studies, semiconductors, mineral exploration, and other branches of science and technology where it is of interest to determine very low concentrations of specific nuclides.

Internationally, the expansion of AMS research has been fuelled by the conversion and redesign of existing nuclear physics accelerators and by the development of low-voltage facilities dedicated to radiocarbon dating. AMS applications are contributing to a vast array of high priority issues related to global climate, environmental pollution, public health and international safeguards of nuclear materials.

A comprehensive review of the technique of AMS and its areas of application is given in (Tuniz et al., 1998).

2. AMS analysis

AMS incorporates an ion accelerator and its beam transport system as elements of a mass and charge

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Table 1
The principal long-lived radionuclides measured by AMS

Radioisotope	^{10}Be	^{14}C	^{26}Al	^{36}Cl	^{41}Ca	^{129}I	^{236}U
Half-life (My)	1.51	0.00573	0.705	0.301	0.103	15.7	23.4
Stable isotopes	^{9}Be	^{12,13}C	^{27}Al	^{35,37}Cl	$^{40,42,43.44}$Ca	^{127}I	^{235,238}U
Stable isobars	^{10}B	^{14}N[a]	^{26}Mg[a]	^{36}Ar[a], ^{36}S	^{41}K	^{129}Xe[a]	—
Chemical form	BeO	C	Al_2O_3	AgCl	CaH_2 CaF_2	AgI	U_3O_8 U + Fe_2O_3
Min sample	0.5	0.02	2	1	20	2	10
size (mg)					1		0.002
Sensitivity[b] (isotopic ratio)	2×10^{-15}	0.8×10^{-15}	2×10^{-15}	1×10^{-15}	5×10^{-15} 5×10^{-13}	5×10^{-14}	2×10^{-11} 10^{-8}
Detection limit (atoms/sample)	10^5	2×10^4	10^5	10^5	10^6	10^6	10^8

[a] Do not form negative ions.
[b] The values given for abundance sensitivity (isotopic ratio of radioisotope/stable isotope) are the best typically achieved at AMS laboratories. However, this sensitivity is generally not achievable with the minimum sample size listed. The detection limit in terms of atoms per sample is calculated using the sample mass required to achieve the best sensitivity.

spectrometer. Multiple selection stages for energy, momentum, velocity and atomic charge plus final identification of nuclear mass and charge with an ion detector make possible the 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 (see Table 1). In addition, the efficiency of AMS in the detection of long-lived radionuclides is 10^6–10^9 times higher than decay counting and the size of the sample required for analysis is reduced accordingly. For example, ^{14}C has been analysed in organic samples containing less than 10 μg carbon.

2.1. Choice of accelerator

Electrostatic tandem accelerators are the optimum choice for a variety of AMS applications.

Tandem accelerators with a terminal voltage of 0.5 MV have been recently designed for ^{14}C analysis. Low-energy tandems (2–3 MV) can be used to detect long-lived radionuclides, such as ^{10}Be, ^{26}Al and ^{129}I. Larger tandem accelerators (> 5 MV), originally developed for nuclear physics research, are used to analyse a variety of rare radionuclides. In this case, higher energies allow an effective separation of isobaric interferences and radionuclides such as ^{36}Cl and ^{41}Ca can be detected in natural samples.

Other accelerators, e.g. cyclotrons, were used for early AMS attempts to measure long-lived cosmogenic radioisotopes. AMS systems based on small cyclotrons are being developed to detect ^{14}C at natural abundances, but their practical use will require further developments to allow precise measurements of isotopic ratios. Linacs with positive ion sources have been applied for the detection of long-lived radioisotopes of noble gases such as ^{39}Ar and $^{81-85}$Kr.

2.2. AMS with tandem accelerators

Negative ions are produced in a sputter ion source and, after energy and mass analysis, are injected into the tandem accelerator. High precision AMS measurements are carried out by using either simultaneous injection or rapid sequential injection of the isotopes of interest. After their injection, negative ions are attracted by the positive voltage at the terminal and thereby accelerated to energies of 0.5–15 MeV, at which point they pass through a gas or a carbon stripper foil and are stripped of some of their electrons. Multi-charged positive ions are then further accelerated by the same positive voltage on the terminal. The stripping process is used to intercept all the molecular interferences, which constitute the main limitation for conventional mass spectrometry. After the acceleration stage, double focussing magnets, Wien filters, electrostatic analysers and gas-filled magnets provide the selectivity necessary to separate the radioisotope of interest. Finally, identification of the rare isotope is performed in the ion detector. Depending on the isotopes to be analysed, 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 are measured to identify the isotopes of interest. New approaches based on selective laser induced ionisation and detection of ion induced X-rays are being attempted to separate isobaric interferences.

3. AMS applications

Long-lived radionuclides are used as tracers and chronometers in many disciplines, including environ-

mental science, archeology and biomedicine. The significance of AMS applications in these areas are briefly discussed in the following. Most examples are related to studies performed at the Lucas Height AMS facility in Sydney, Australia.

3.1. Palaeoenvironment

The Quaternary period covers the last two million years of terrestrial history. It is significant because within this time frame there were great climatic upheavals and humankind spread across the world. Quaternary science includes a variety of scientific disciplines such as biology, climatology, geography and geology, providing the knowledge needed for reconstructing the past of the environmental conditions on the global scale.

Cosmogenic radionuclides provide radiometric clocks to establish an absolute time scale for the environmental events of the Quaternary period and AMS is the analytical method of choice for their analysis.

Sediments, tree rings, polar ice and rocks serve as archives of the environmental conditions in the past to study changes in the natural system.

3.1.1. Sediments

Ancient sediments archive environmental events, such as climatic changes, that have taken place in the past before the existence of instrumental records. ^{14}C analyses by AMS of microscopic samples from charcoal, pollen and other organic materials provide the time scale for the last 50,000 years. ^{10}Be in sediments can be used to extend this chronology providing time markers related to reversals of the geomagnetic field or other processes that affect the production of cosmogenic radionuclides during the Quaternary period.

The Earth's environmental systems have undergone many changes and investigating these provides insight into how environmental changes are driven and the effect they have on the biosphere. Australia has many of these kinds of archives and they can help us to understand how global scale environmental changes have been expressed in the biota and palaeo-hydrology of the continent. These records can then be used to help identify the kinds of forcing factors that influence the climate and the sensitivity of vegetation to environmental changes.

Major research projects are under way in Australia to understand the late-Quaternary history of vegetation, fire and climate. Some of these projects aim to investigate how very high bio-diverse vegetation in Australia responds to change, and the bearing of this in relation to the maintenance of high bio-diversity. Records of vegetation change, fire history, land clearance and land-use in relation to the onset and development of salinity in lakes are being reconstructed.

Table 2
Typical sample size required for ^{14}C dating of archaeologically significant materials

Material	Quantity[a]	Material	Quantity[a]
Wood	5	Shell, carbonates	10
Bone	500	Paper, textiles	5–10
Charcoal	3–5	Grass, seeds, leaves, grains	5–10
Beeswax	1–2	Hair, skin	5–7
Pollen	1	Teeth, tusk, ivory	500–700

[a] Milligrams for AMS, grams for decay counting.

Other Australian research programmes involve the examination of sea-level change and deglaciation chronologies from Antarctica, freshwater stromatolites in Southern Australia and vegetation histories derived from lake sediment cores from Tasmania.

Dating techniques that yield high-precision age estimates of these terrestrial archives are essential. The AMS ^{14}C dating technique is well suited to the sort of organic materials encountered in this research. As a technique capable of measuring ^{14}C levels in sub-milligram samples, AMS ^{14}C dating is the only option available when trace amounts of datable material are preserved. In addition, many samples dated from lake and swamp sediments are contaminated by mobile humic acids that cannot be removed totally. Although AMS dating of specific organic fractions refines the radiocarbon analysis, a more secure approach is provided by the direct dating of pollen extracts from the samples (Table 2).

3.1.2. Tree rings

Ancient conifer logs exhumed from the bed of the Stanley River in Western Tasmania range in age from Last Interglacial to the present and have been sampled for dendrochronological and atmospheric ^{14}C studies. The high sensitivity of AMS makes possible ^{14}C analyses in individual tree rings.

The main significance of this research programme lies in the remarkable length of the tree-ring chronology being developed for the Stanley River, with year-by-year precision. The interpretation of climatic change from the tree-ring widths, and the determination of radiocarbon variations from wood tied to this chronology, will contribute much to our understanding of major and abrupt climatic changes during the last deglaciation (15,000–11,700 years ago). Much can be learnt about the subtle style of climatic variations dating from this period, and changes in ocean currents and convection patterns before and after the sea-level stabilised to present levels (around 7000 years ago). Changes in recent centuries can be determined with annual precision from tree rings in the tropical regions in Australia and Southeast Asia, and are highly relevant to studies of the

monsoon system which brings rain from the northern Indian and western Pacific Oceans to these two regions, in alternate seasons each year.

3.1.3. Ice cores

Ice cores provide 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, provide a high-resolution record 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 CSIRO and Antarctic Division, we used the ^{14}C "bomb spike" to determine the age spread and age of CO_2 in Antarctic ice and firn. The sensitivilty of AMS is essential for these analyses, as only 10–20 μg of carbon are available from 1 kg of ice (corresponding to a one-year layer of ice).

Profiles of long-lived cosmogenic radionuclides, as a function of depth and thus age, provide key information on past solar variability, production rate changes, and atmospheric transport and deposition mechanisms.

For example, ^{10}Be, cosmogenically produced in the atmosphere and deposited in ice cores, varies in concentration in a way that correlates with the 11-year sunspot cycle and the sunspot-free period known as the Maunder Minimum (1650-1700 AD). ^{10}Be can be measured by AMS in 1 kg of ice, while one ton of ice would be necessary with conventional techniques

3.1.4. Rocks

Cosmogenic radionuclides such as ^{10}Be, ^{26}Al and ^{36}Cl produced in rocks can provide information on glacial histories in the southern hemisphere. Although only a million atoms of a specific radionuclide are produced during a 100 ka exposure period per gram rock, AMS can be applied to measure this telltale signal. The ANSTO research programme targets three geographic regions that show distinct glacial formations and deposits: Tasmania, New Zealand and Antarctica. The ANTARES AMS spectrometer is used to analyse glacially polished bedrock surfaces, large erratics and boulders deposited on lateral and terminal moraines and within glacial outlet valleys. A number of ice cap advances during the Quaternary have been identified from the radionuclide signals. This study involves also the search of the Younger Dryas (11–13 ka BP) in the southern hemisphere. This is a major short term reversal during the last deglaciation which appears throughout the climatic records of the northern hemisphere.

3.1.5. Oceans

The accelerator analysis of radiocarbon in ocean waters helps to understand the influence of ocean circulation on the world's climate. The Southern Ocean has a key role in the global climate as a source region for water masses and it is important to determine its contribution towards the ventilation of the world ocean, and to quantify its performance as a sink for anthropogenically produced greenhouse gases. The database from oceanic field observations available for model validation purposes is sparse, and the role of the Southern Ocean within the global carbon cycle represents, to date, the largest unknown quantity in discussions of an anthropogenically enhanced greenhouse effect.

Water samples from locations within the Australian sector of the Southern Ocean were obtained to determine their ^{14}C content. The determination of the ^{14}C distribution as a function of depth and location is necessary to validate predictions obtained from the tracer model which was developed for the world ocean region south of 24°S. Subsequently, this model is applied to integrate the observed ^{14}C distribution in space and time, and to establish a ^{14}C budget for the Southern Ocean.

3.2. Archaeology

^{14}C dating provides an absolute time scale for human history over the last 50,000 years. Accelerator mass spectrometry, with its capacity to analyse ^{14}C in sub-milligram carbon samples, has enormously expanded the applicability of this dating method. Specific molecular compounds extracted from ancient bones, single seeds and other microscopic carbon-bearing substances of archaeological significance can now be dated, increasing the sensibility and reliability of the chronological determination.

A few years ago, the AMS analysis of specific aminoacids of human bones at the University of Arizona, confirmed the view that the North American continent was populated about eleven thousand year ago, when an ice-free land corridor was opened across the Bering Strait at the end of the last ice age. More work is needed to support these theories as the validity of AMS ^{14}C dates on poorly preserved fossil bones remains questionable.

Palaeoanthropologists are interested in the origin of *Homo sapiens sapiens* in Europe and its relation to the hominids of the Neanderthal type. AMS has been used to date bones from the Upper Pleistocene Europe.

Concerning the first colonisation of Australia, until recently, the most ancient radiocarbon dates for the human presence in Australia corresponded to less than

40,000 BP, as shown by AMS dates from the Kimberley region. Recent ESR and U-series dating investigations on the three human skeletons of Lake Mungo yielded a date of $62{,}000 \pm 6000$ BP, in good agreement with OSL age estimates on the sediments into which the skeleton was buried ($61{,}000 \pm 2000$ BP).

Thanks to the very limited invasiveness of AMS, rare artefacts can be sampled for dating without undue damage. Through the analysis of famous artefacts and findings such as the Shroud of Turin, the Ice Man, the Dead Sea Scrolls and the Crown of Charlemagne, AMS has gained widespread public recognition as a dating technique.

3.3. Life sciences

^{14}C has been used extensively as tracer in biology and medicine. In general, limitations of counting methods forced experiments to be carried out with high chemical and radioactive doses. AMS offers a number of advantages for applications of radioiosotopes as tracers in the life sciences (see Table 3):

(i) the ability to determine radioisotopes in μg to mg amounts of sample reduces the quantity of tracer that must be administered and the amount of material that must be extracted for analysis by many orders of magnitude; repeated measurements can be made on the same tissue;
(ii) the ability to determine enhanced levels of radioisotope in minutes of measuring time increases the number of samples that can be analysed and hence the detailed information that can be derived;
(iii) the half-life of the radioisotope is not relevant in AMS because the number of atoms rather than the number of decays is measured, so that there is a wider choice of tracers available for the study of biomedical processes; although not yet demonstrated, stable isotope determination with exceptional sensitivity by AMS;
(iv) radiation hazards to the subjects and researchers are reduced by both the small sample and the long half-life capabilities; AMS measurements have already been made of the uptake of long-lived radioisotopes by human volunteers and the use of doses well below accepted radiation limits as well as non-invasive sampling may eventually become routine in clinical studies;
(v) due to the enhanced AMS sensitivity, long-term biomedical studies, of the order of many months or years, are possible.

A considerable number of experiments have confirmed these advantages and biomedicine is set to become a major field of application of AMS. A few specific AMS applications are related to toxicity, drug testing, pharmacokinetics, Alzheimer's disease, etc. Concerning toxicity, perhaps the most significant aspect of work to date is the study of biological response to toxins at environmentally relevant dose levels. Large uncertainties can arise in extrapolating effects from high dose experiments to natural dose levels which can mask the important distinction between threshold effects, non-linear or linear responses.

Table 3
Isotopes for biomedical applications

Isotope	$T_{1/2}$	Sensitivity	Applications
^{3}H	12.3 a	10^{-14}	General
^{7}Be	53 d	10^{-15}	Metabolism, toxicology
^{10}Be	1.5×10^{5} a	2×10^{-15}	Metabolism, toxicology
^{14}C	5730 a	1×10^{-15}	General
^{26}Al	7.1×10^{5} a	2×10^{-15}	Metabolism
^{32}Si	140 a	10^{-13}	Bone
^{36}Cl	3.02×10^{5} a	1×10^{-15}	Metabolism
^{41}Ca	1.04×10^{5} a	2×10^{-15}	Bone
^{53}Mn	3.7×10^{6} a	10^{-10}	Metabolism
^{60}Fe	1.5×10^{6} a	10^{-12}	Metabolism
^{79}Se	6.5×10^{4} a		Metabolism
^{129}I	1.5×10^{7} a	5×10^{-14}	Metabolism

3.4. Nuclear non-proliferation

The international safeguards system has been developed to ensure that nuclear materials are not diverted from declared activities and that undeclared activities have not occurred. The main task of International Atomic Energy Agency (IAEA) safeguards is the verification of the correctness and completeness of declarations made by states under relevant agreements. Traditionally, safeguards methods are based upon nuclear accounting and surveillance techniques. Environmental sampling and analysis has recently been introduced by the IAEA as part of the strengthened safeguards system.

Plutonium or highly enriched uranium (HEU) is the ingredient needed for the construction of nuclear weapons. Reactor operations and reactor activities for the production of plutonium would have the effect of releasing a wide range of fission products and actinide isotopes into the surrounding environment. The disturbance of uranium isotopic ratios would be the most evident signature.

ANSTO has participated in IAEA-sponsored field trials to determine the distribution of the long-lived fission product ^{129}I from the environs of a reprocessing plant. AMS provides the most sensitive available technique for the detection of rare long-lived radioisotopes like ^{129}I, with a detection limit of one million atoms or less, even in the presence of abundant stable

isotopes of the same element. A range of possible radioisotopes detectable by AMS have been considered for use in safeguards applications, including ^{14}C, ^{36}Cl, ^{129}I and actinides. These radionuclides can be used to trace specific nuclear activities: reactor operations and nuclear explosions (^{14}C, ^{36}Cl, ^{129}I, ^{3}H), fuel reprocessing (^{129}I, U–Pu) and uranium enrichment (U isotopes).

Determination of the origin of uranium samples is of great interest in verifying correctness and completeness of declarations. The ratios of uranium isotopes have been suggested as a possible means of 'fingerprinting' uranium materials. The three naturally occurring uranium isotopes with long half-life, ^{234}U, ^{235}U and ^{238}U, occur with ratios that have small variations depending on the geographic origin, due to isotopic fractionation or other effects. ^{236}U might show a wider variability due to its sensitivity to the local neutron flux, but its concentration is often at the fringe of the detection limit for conventional mass spectrometry.

The isotopic disturbance of ^{236}U in the environment has been suggested as a powerful signal to identify specific nuclear activities, such as reprocessing of nuclear fuels. The $^{236}U/^{238}U$ ratio in natural samples can be as low as 10^{-10} at/at, while nuclear materials exhibit $^{236}U/^{238}U$ ratios at the level of 10^{-2} at/at. Therefore, anthropogenic ^{236}U may be detectable above natural levels in environmental samples such as soils, water, biota and atmospheric particulates.

With a current detection limit of $^{236}U/^{238}U < 10^{-11}$, AMS can complement conventional techniques such as Thermal Ionisation Mass Spectrometry, particularly because of its extremely high abundance sensitivity and wide dynamic range.

4. The future of AMS

Applications of AMS methods in quaternary and environmental sciences will expand further in the foreseeable future with long-lived cosmogenic radionuclides contributing to a large body of knowledge on processes involving atmosphere, oceans, ice sheets, biosphere, soils and sediments. In particular, radionuclides produced in situ in exposed rock and surfaces will be increasingly used as geochronometers and tracers of various geochemical and geophysical surface modification processes.

Biomedicine is set to become a major direction for future AMS applications, particularly in applications investigating biological responses to toxins at environmentally relevant does levels.

Finally, a range of possible radioisotopes detectable by AMS are being considered for use in safeguards applications, including ^{99}Tc, ^{129}I, ^{236}U and other actinide isotopes.

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