

# ACCELERATOR MASS SPECTROMETRY: AN ANALYTICAL TOOL WITH APPLICATIONS FOR A SUSTAINABLE SOCIETYS

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## Abstract

Accelerator Mass Spectrometry (AMS) adds the techniques of charged particle acceleration to the basic principles of Isotope Ratio Mass Spectrometry (IRMS) to provide extremely low detection capability (below 1 femtogram) of rare isotopes in samples of natural materials as small as 1 mg. Depending on the element selected and the configuration of the equipment, sensitivities can reach one part in  $10^{15}$ . The advantages of this small sample size and high sensitivity include the economic benefit of collecting, shipping and preparing much smaller samples, and also the ability to analyse specific chemical compounds within the sample, so that the pathway taken by that compound through complex systems can be more precisely traced or, in the case of radioactive isotopes, more precise chronological information can be provided. The paper begins with a basic overview of AMS technology, with an emphasis on how the use of higher energy contributes to this enhanced sensitivity, then provides several examples of new AMS technologies which reduce the energy and space requirements for such systems, and follows with several examples of applications which contribute to the investigation of sustainability in other areas of environmental concern.

## 1. INTRODUCTION

### 1.1. Requirements leading to the development of AMS

The use of accelerators to increase the sensitivity of mass spectrometry has had a long history, dating back to 1939 when Alvarez and Cornog used the recently developed Berkeley cyclotron to identify the existence of  $^3\text{He}$  in a sample of  $^4\text{He}$  at a ratio of  $^3\text{He}/^4\text{He} \approx 1 \times 10^{-6}$  [1]. However, such measurements remained isolated experiments until the development of tandem electrostatic accelerators [2] and the negative ion sources needed to provide anions from solid, rather than only gas samples [3]. During this time, the technique for measuring the age of organic samples developed by Libby [4] using the counting of  $\beta$  particles from the decay of  $^{14}\text{C}$  in the sample was gaining widespread use in the fields of Earth and environmental science as well as in Archaeometry as the half-life of  $^{14}\text{C}$  (5730 a) permitted good chronological measurements for late Quaternary geological events and for the development of human societies. By the mid 1970s, the demand for precise and rapid  $^{14}\text{C}$  dating was exceeding the capacity of the decay-counting method, even with improvements of newer technology, such as liquid scintillation counting. Mass spectrometry at this time was still hindered by the overwhelming presence of the isobar  $^{14}\text{N}$  with very nearly the same mass ( $\Delta M/M = 3.06 \times 10^{-4}$ ). This barrier was overcome in 1977 by Purser et al [5], who showed that the negative ion of  $^{14}\text{N}$  (needed for injection into tandem electrostatic accelerators) is unstable whereas that of  $^{14}\text{C}$  was relatively robust. This was followed quickly by several papers demonstrating the use of tandem electrostatic accelerators, equipped with Middleton type caesium sputter ion sources [3], to provide  $^{14}\text{C}$  measurements with acceptable accuracy [6,7]. The two key technical requirements: ion energy provided by the tandem accelerator and high ion currents from the sputter source were now in place

### 1.2. Expansion to applications beyond $^{14}\text{C}$

Following this initial discovery, the number of isotopes which could be easily analysed expanded rapidly:  $^{10}\text{Be}$  [8],  $^{36}\text{Cl}$  [9] and  $^{129}\text{I}$  [10]. Within another decade, these included the actinides [11] and, for example, a less abundant isotope  $^{236}\text{U}$ . In the over 40 years of the availability of AMS analyses, many applications in Earth, environmental, planetary, biomedical and cultural sciences have been developed. Of particular interest to sustainability are the contributions made to climate change research using  $^{14}\text{C}$  and more recently  $^{26}\text{Al}$ ,  $^{36}\text{Cl}$  and  $^{10}\text{Be}$ , to provide details about previous climate change events and to monitor the specific events associated with current changes, such as permafrost thawing, sources of atmospheric methane, or carbon cycling in the oceans.

For the energy sector, atmospheric measurements of  $^{14}\text{C}$  are used to assess the efficacy of bio-remediation programs for fossil fuel spills and the actinides and fission fragments are analysed to monitor the production, use and disposal of nuclear fuel. Cultural applications include collaborations with indigenous communities to provide chronologies for events chronicled in oral histories, some of which include their adaptation to earlier environmental changes.

### 1.3. AMS and Sustainability

There are currently approximately 160 AMS systems in operation throughout the world, ranging in acceleration voltage from 200 kV to 15 MV, a number which has doubled in the past 10 years. However, as the space and cost of such equipment scales with the terminal voltage, manufacturers and many of their clients are opting for smaller systems. Those which operate at the lowest of these voltages are specifically designed for one element (typically carbon isotopes), which permits the use of permanent, instead of electro-magnets – a significant saving in operating costs. In addition, there are a number of multi-element machines coming on line which operate at 300 kV. In both cases, these systems can be equipped with integrated sample preparation equipment, such as elemental analysers, carbonate analysis systems or even IRMS systems for abundant stable isotope analyses of the same sample – a further economy in labour and time.

## 2. TECHNIQUES WHICH ENABLE AMS SENSITIVITY

### 2.1 Challenges and Solutions

The requirement to measure isotope ratios at very low concentrations (typically 1 part in  $10^{12} - 10^{15}$ ) sets AMS apart from IRMS in several ways:

- An increased presence of isobars (atoms or molecules of a different element which have a mass so close to the mass of the rare isotope of interest that they are not resolvable by conventional mass analysis techniques, such as magnet-electric analyzer combinations or radio-frequency quadrupoles (RFQs)) The initial solution provided by AMS, as described in section 1.1, is the use of negative ions. However, this solution provides only a few, albeit important solutions –  $^{14}\text{C}$  ( $^{14}\text{N}$ ),  $^{26}\text{Al}$  ( $^{26}\text{Mg}$ ) and  $^{129}\text{I}$  ( $^{129}\text{Xe}$ ). For molecular isobars, the accelerator provides the energy necessary to break up the molecules in the accelerator terminal electron stripping canal (see Figure 1). For other atomic isobars, the accelerator provides the energy required to use energy loss methods such as energy degrader foils or gas-filled magnets. These combined with a gas ionization detector can, with sufficient energy, resolve most isobar issues.
- The low concentration of the rare isotope of interest, as well as the increasingly smaller samples that require analysis require an ion source which can efficiently generate high currents. For example, whereas an IRMS instrument can provide precise results with a nano-ampere beam of analyte ions, an AMS source requires 10s to 100s of micro-amperes to provide rare isotope analyses with sufficient precision to achieve statistical precisions of between 1% and 1‰. These are typically sources which sputter solid samples with a high current of  $\text{Cs}^+$  ions, but some systems are now using electron cyclotron resonance (ECR) sources and charge changing where necessary.

### 2.2 Basic Parts of an AMS system

As most AMS systems still use tandem electrostatic accelerators, the technique will be illustrated using such systems. Some smaller systems use only a single high voltage acceleration gap as indicated in ref [13], but many of the principles are common to both approaches. The main parts of a tandem accelerator-based system are summarized in Fig 1.

The low energy spectrometer section, which includes the ion source, an electric analyser to select a precise ion energy (if needed) and an injection magnet which selects the ions of a specific momentum. Together these two elements define the mass selected for injection. Most systems include a method for rapid switching between the rare and abundant isotopes, usually by accelerating or decelerating either the rare and/or abundant ions before and after the magnet, thus adjust the ion momentum appropriately.

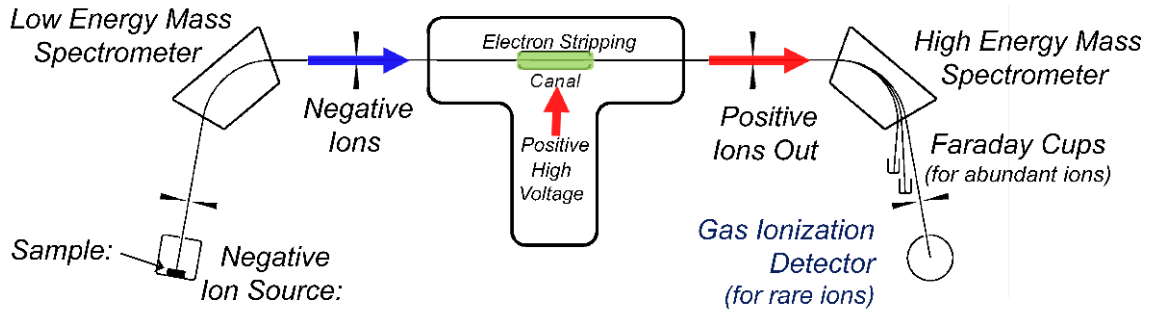


Figure 1: Basic parts of an AMS system using a tandem electrostatic accelerator

The accelerator section includes the high voltage power supply, graded vacuum tubes to conduct the ions to and from the high voltage terminal and an electron stripping device in the terminal. This can be either a foil or a windowless gas cell, with a pump to recirculate the stripping gas. This removes electrons from the incoming beam and provides positive ions for further acceleration. With sufficient foil thickness or gas pressure and appropriate ion velocity, molecular ions can be disintegrated into their constituent atoms and the charge state of the positive ions can be optimized to facilitate further analysis.

The high energy spectrometer section includes the magnets and electric analysers required for the analysis of the positive rare ion beam as well as Faraday cups, usually following the first magnet, to measure the current of the abundant beam(s) and a gas ionization or silicon detector to count the positive rare ions. The gas ionization detector provides extremely low noise, single atom counting as well as energy loss information, which can be useful in further isobar discrimination. A particular implementation of these sections is shown in Fig 2, a schematic of the AMS system at the Lalonde AMS Lab in Ottawa.

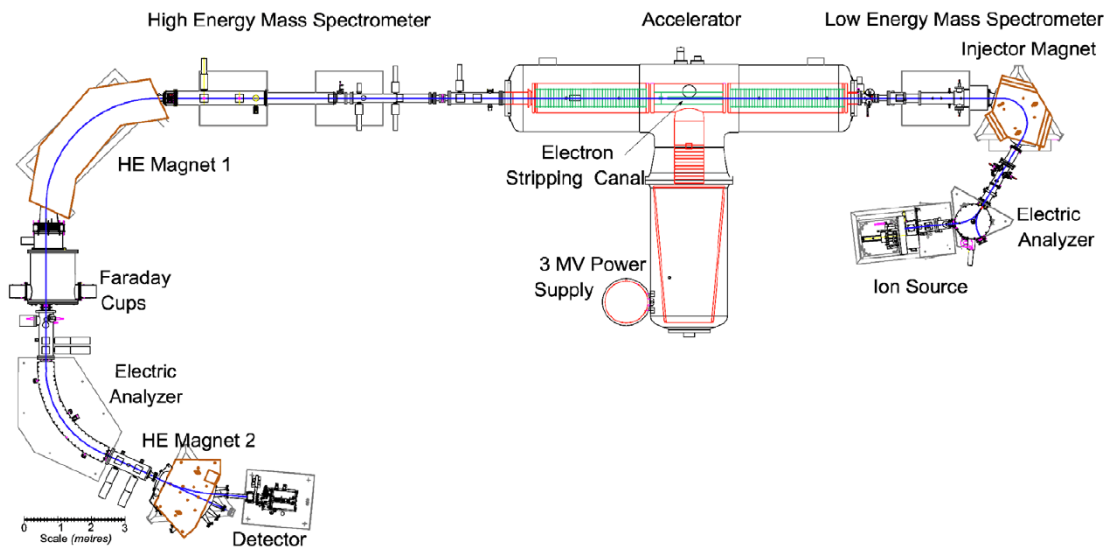


Figure 2: The AMS system at the Lalonde AMS Lab, University of Ottawa. Due to building constraints, the ion beam direction is from right to left.

### 3. SUSTAINABILITY IN AMS TECHNOLOGY

#### 3.1 Smaller AMS Systems.

Accelerator manufacturers, in some cases for over a decade, have been building smaller AMS systems, which require significantly less space (a capital cost reduction) as well as less electrical power for their operation. These can be broadly divided into two types:

- Low energy tandem accelerators, using high voltage terminal voltages of between 200 and 300 kV [14, 15]. Due to the shorter distance to the accelerator terminal, such instruments often provide better transmission efficiency through the accelerator than their larger counterparts
- Single stage AMS systems in which either the high energy (more usual) or the low energy spectrometer section is placed on a high voltage platform [13, 16]. These systems, with only one short accelerator tube also exhibit enhanced transmission efficiency.

### 3.2 Single Element AMS systems.

In larger systems, magnets typically consume the most power (more than the accelerator) Systems built for specific isotope analysis (e.g.,  $^{14}\text{C}$ ), can use permanent magnets with a small coil for minor adjustments. In addition to conserving electrical power, such magnets eliminate the need for water cooling of the coils, necessary for a conventional electromagnet.

An example of a single element system for  $^{14}\text{C}$  (MICADAS<sup>TM</sup> Ionplus AG) recently installed at the Lalonde AMS Lab, is shown in Fig 3 and the high energy permanent magnet in Fig 4 below.



Figure 3: Single Element  $^{14}\text{C}$  System installed at Lalonde AMS



Figure 4: High Energy Permanent Magnet with upper yoke lifted during assembly. Note the small size of the trim coil compared with the space available for a water-cooled full power coil.

## 4. EXAMPLES OF APPLICATIONS PROMOTING SUSTAINABILITY IN OTHER FIELDS

### 4.1 Carbon in the Arctic Environment

It is now well established that the Arctic (and the Antarctic) regions are experiencing the effects of almost a doubling of the current increase in global average temperatures. In terms of carbon storage or emission, this represents a “two-edged sword”, as although the reduced ice cover in the ocean regions permits an increase in biological carbon sequestration in the water column and the sediments, this could easily be overwhelmed by the thawing of permafrost regions with a release of methane as well as carbon dioxide.

AMS carbon isotope analysis has played an important role in the testing of models predicting sea-level rise and glacial isostatic adjustment [17] as the timing of the changes since the last glacial maximum (~203 ka B.P.) matches well the half-life of  $^{14}\text{C}$ . On-going studies of carbon in the water column [18] and sediments [19] already providing information about the region’s response to previous climate changes.

The small sample AMS capability will increase the use of Compound Specific Radiocarbon Analysis (CSRA). The original intention of this approach was to reduce the possibility of heterogeneous sources of  $^{14}\text{C}$  in samples. While recent work [20] have shown that this is not necessarily the case the technique can be improved by reducing the size of the samples. The increased efficiency of the new smaller AMS systems is expected to contribute to further developments of this technique.

## 4.2 Bio-remediation of hydrocarbon spills

The process of using naturally occurring bacteria to remediate sites where hydrocarbon fluids have been spilled or leaked into the ground is monitored by analysing the carbon isotope ratio of the CO<sub>2</sub> released with other soil gases. If the CO<sub>2</sub> is modern or nearly so, the bacteria are not processing the hydrocarbons, but more recently formed deposits, such as forest fire debris. To analyse a soil gas sample directly requires a large gas volume, an expensive and cumbersome collection, handling and shipping process, as well as further processing by the AMS lab.

In an alternative method [21], by passing the soil gas through a filter bed of Ba(OH)<sub>2</sub>, the CO<sub>2</sub> reacts with the Ba(OH)<sub>2</sub> and produces BaCO<sub>3</sub>. Filter cartridges can simply be loaded with Ba(OH)<sub>2</sub> in a local lab and are used by commercial operators to test remediation sites. Exposed filter cartridges are economically returned to the AMS lab and can be analysed using an automated Carbonate Handling System connected directly to the AMS ion source.

## 5. SUMMARY

For almost 45 years, AMS has provided highly sensitive isotope analyses for Earth, environmental, archaeometric, bio-medical and materials sciences. New AMS systems and techniques are being developed which require less energy, space and sample preparation time. Applications continue to be developed which are making an impact on research that is important for the sustainability of our society.

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