

AMS facility at Institute of Physics, Bhubaneswar: Inter-laboratory comparison of results

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Radiocarbon dating has found wide applications in many areas of science like archaeology, geology, oceanography, palaeoseismology and palaeoclimatology. As a tracer, radiocarbon has applications in biology and medicine. Radiocarbon dating using Accelerator Mass Spectrometry (AMS) provides several advantages over the conventional decay counting method. The first AMS facility in India for radiocarbon dating has become operational at the Institute of Physics, Bhubaneswar. This note describes the operational features of this facility and inter-laboratory comparison of data.

Keywords: Accelerator Mass Spectrometry, carbon isotope, radiocarbon dating.

Radiocarbon dating developed by W. F. Libby is used to date carbon-containing materials, as old as 50,000 years. The radioactive isotope ^{14}C is produced by interaction of nitrogen with secondary neutrons produced by cosmic rays in the upper layers of the atmosphere. Oxidized ^{14}C mixes with the atmospheric CO_2 and is eventually incorporated in all living organisms at a concentration corresponding to equilibrium between its production and decay rates. After the death of an organism, exchange of $^{14}\text{CO}_2$ with the biosphere ceases, and hence the equilibrium concentration begins to decrease exponentially by radioactive decay with a half-life of 5730 years. By measuring the residual concentration of ^{14}C relative to that of stable isotopes ^{12}C (98.89%) and ^{13}C (1.11%), the age of the sample can be determined. The ratio of $^{14}\text{C}/^{12}\text{C}$ in modern biogenic carbon is $\sim 1.2 \times 10^{-12}$.

The advantage of Accelerator Mass Spectrometry (AMS) over the conventional decay counting technique is that it can measure ^{14}C atoms directly, whereas the latter is based on counting beta particles following the decay of ^{14}C atoms. Thus AMS requires only about a milligram of the sample and about 30 min per measurement. In comparison, the decay counting method requires not less than a gram of the sample and several hours to days of measurement for a reasonable statistical precision. AMS has a sensitivity of better than 1 in 10^{15} . There are about 130 laboratories in the world using the conventional decay counting method, but only about 25 laboratories using AMS.

The 3 MV NEC model 9SDH-2 tandem accelerator in the Institute of Physics (IOP), Bhubaneswar has been a major experimental facility for over 12 years in

materials science research and other applied fields. This machine has been augmented for operation as a national AMS facility for ^{14}C dating under a project jointly funded by DST, DOS, DAE and CSIR. Technical modifications and additions to the basic accelerator and operational parameters are given in Mahapatra *et al.*^{1,2}. The layout of the AMS facility is shown in Figure 1. The pre-acceleration section consists of an MC-SNICS ion source, an electrostatic analyser (ESA) and an injection magnet. The tank in the middle houses the tandem accelerator. The post-acceleration section comprises an analysing magnet, a switching magnet and a beam line exclusively for AMS use, consisting of a magnetic quadrupole, an ESA and a detector chamber.

Sample preparation

For AMS dating, the sample needs to be converted to carbon (graphite) form. The sample material (e.g. wood, charcoal, peat, shell) is pretreated using standard wet chemical methods for removing extraneous carbon contamination. After pretreatment, the sample material is converted to CO_2 either by reaction with phosphoric acid in the case of carbonates (e.g. shell, foraminifera, etc.) or by combustion in a quartz tube with CuO at $\sim 1000^\circ\text{C}$ in vacuum. The CO_2 is then reduced to graphite with H_2 gas using iron powder as catalyst at 630°C . The graphite deposited on iron powder is then pressed into an orifice in aluminum sample holders. The graphite preparation system² was develo-

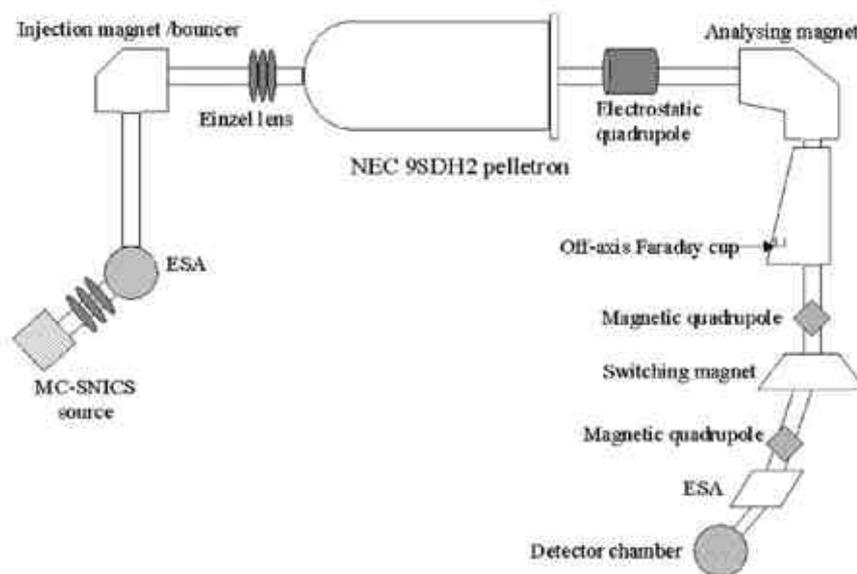


Figure 1. Schematic of the accelerator layout and AMS beam line at IOP.

ped at the Physical Research Laboratory, Ahmedabad and reassembled at the IOP with further improvements. Several shell and other inorganic carbonate samples have been processed using the acid hydrolysis method. Sample quantity required to prepare 1 mg of graphite is less than 10 mg for most of the inorganic samples mentioned above. A combustion unit for processing organic carbon samples is being set up.

AMS analysis procedure

In the AMS method, carbon isotopes are accelerated to energies of the order of a few MeV energies and mass separated. ^{14}C ions are counted using a particle detector, while the far more abundant ^{13}C ions are measured as electrical current in an off-axis Faraday cup. The age of a sample is determined by comparing its $^{14}\text{C}/^{13}\text{C}$ ratio with that of a standard of known ratio.

The multi-cathode cesium sputter negative ion source MC-SNICS can hold 40 samples. When a sample is selected for analysis, negative ions of carbon isotopes are produced in the source and pre-accelerated to nearly 50 keV. The electro-static analyser (ESA) allows only the ion beam of specified energy to pass through. This beam is then mass analysed by the injection magnet to facilitate injection of the selected mass (13 or 14) into the main accelerator. The terminal voltage of the accelerator is set to 2.36 MV. Beams of ^{13}C (stable isotope) and ^{14}C (radioactive) isotope are sequentially injected into the accelerator for measurement. Initially the magnetic fields of injection, analysing and switching magnets are all set for ^{14}C transmission. Sequential injection of both the beams is achieved by applying high voltage pulses of about 4 kV to the injection magnet chamber. When the voltage is off, $^{14}\text{C}^-$ is injected and when the voltage is on, the $^{13}\text{C}^-$ beam is injected. Typical injection times are 5 s for ^{13}C and 30 s for ^{14}C . The injected negative ions undergo collisions with argon gas atoms at the high voltage terminal of the accelerator, and become positive ions due to electron-stripping. For the terminal potential of 2.36 MV, the most probable charge state of the stripped ions is 3+. After acceleration, the beams are mass-analysed by the analysing magnet. The $^{13}\text{C}^{3+}$ beam is measured in an off-axis cup situated between the analysing and switching magnets. The $^{14}\text{C}^{3+}$ ions with 9.5 MeV energy are

deflected by the switching magnet into the dedicated AMS beam line and counted using a particle detector at the end. The 15°ESA in the AMS beam line selects ions of specified energy to pass through and rejects ions of all other energies.

The data acquisition and control system is CAMAC-based and is interfaced with a PC running the Gnu-Linux operating system. The data acquisition program controls the sequential injection of ^{13}C and ^{14}C by applying the bouncing voltage to the injection magnet chamber, reading the $^{13}\text{C}^{3+}$ current from the off-axis cup and counting the $^{14}\text{C}^{3+}$ ions in the detector.

Results

$^{14}\text{C}/^{13}\text{C}$ ratio of unknown samples is measured and compared with those of the NBS oxalic acid reference standards OX-I and OX-II. Background ^{14}C levels are measured using dead carbon in sample holders. Samples already dated by the conventional counting method at the Birbal Sahni Institute of Palaeobotany (BSIP), Lucknow, and by the AMS method at the NSF Arizona AMS facility were analysed using the IOP machine for intercomparison of results. The Arizona samples, as received, were already graphitized and pressed into sample holders. The results are presented in Table 1. Sample numbers prefixed with T are from Arizona and those with prefixes S and BS are from the BSIP.

As can be seen from Table 1, there is, in general, good agreement between our results and those of the two laboratories on the same samples. However, there are also some discrepancies. The most discrep-

ant results between our data and the other one pertain to samples T14787 and S-3002. In the case of 'younger' samples such as T14787, what is critical in the measurement is the drift in beam tuning between repeated comparisons of sample and standard. Established AMS laboratories have fully automated systems for rapid comparisons between sample and standard, whereas in the IOP facility, samples are changed manually. We could not repeat the measurements on T14787, as it was used up quickly. We expect to implement rapid comparisons between sample and standard soon to reduce the effects of machine drift. Isotopic fractionation is another important parameter that strongly influences the age determination of younger samples. A stable isotope mass spectrometer is being set up to measure the $^{13}\text{C}/^{12}\text{C}$ ratio in the aliquot of sample CO_2 to address this issue. Sample T14782 is the oldest as seen from Table 1. Accurate determination of background counts is critical in dating samples as old as 40,000 years or more. Any small amount of contamination during graphite preparation results in background counts and laboratories try to adopt procedures to minimize this effect. After applying the background correction according to the Arizona data, we determined the age of the sample. It may be noted that background correction can lead to a larger error than the statistical error and hence we have not shown the statistical error on this sample.

Comparing the results of measurements from BSIP and IOP, it may be noted that the methods used are different. BSIP measurements were based on extracting carbon from gram quantities of samples

Table 1. Comparison of radiocarbon dates (in years) between laboratories

Sample	IOP	Others
T14799	14684 ± 210	14719 ± 77
T14795	11511 ± 140	11383 ± 58
T14782	41000	41000
T14787	599 ± 105	1116 ± 38
T14789	5071 ± 165	5227 ± 45
T14791	9010 ± 160	8734 ± 49
T14792	9263 ± 180	9558 ± 55
T14793	11323 ± 160	10364 ± 55
S-2973	4601 ± 140	5080 ± 100
S-2976	5121 ± 120	5500 ± 120
S-2491	11230 ± 400	11490 ± 100
BS-1979	8583 ± 205	8230 ± 130
S-3049	2480 ± 140	2830 ± 220
S-3002	2680 ± 140	7030 ± 320
S-3030	6260 ± 140	5420 ± 80
S-3033	35200 ± 700	35900 ± 1040

in the form of benzene and counting their ^{14}C activity in a liquid scintillation counter. IOP measurements, on the other hand, were on milligram quantities of samples processed to extract graphite and using the AMS to determine their $^{14}\text{C}/^{13}\text{C}$ ratio. Despite substantial difference in methodologies and sample-size requirements, agreement between results from the two laboratories is quite good except in one case, namely S3002. In this case, as the quantity of sample available for the conventional counting method was not sufficient, the BSIP laboratory mixed the sample with a known quantity of dead (inactive) carbon to produce sufficient amount of benzene for scintillation counting (B. Sekar, BSIP, private commun.). While the error quoted (320 years) represents only statistical precision in counting, there could be a large error in subtracting the contribution of dead carbon from the mixture. In conclusion, the agreement of our results with those from the two other laboratories, particularly from Arizona

demonstrates the viability of our facility for ^{14}C dating on par with other AMS laboratories in the world.

To follow up this development, we organized, a two-day User Interaction Meeting on AMS Radiocarbon Dating in August 2004 with the participation of about 40 scientists. About 20 talks were delivered on applications of ^{14}C in geology, palaeoclimatology, palaeoceanography, palaeobotany, palaeoseismology, archaeology, etc. Scientists interested in using our facility are welcome to submit their proposals.

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Fabrication of an inverse photoemission spectrometer to study unoccupied electronic states

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We discuss the performance of an inverse photoemission spectrometer that has been recently fabricated in our laboratory. The photon detector is of band-pass type with acetone gas filling and CaF_2 window (acetone/ CaF_2). We determine the optimal operating conditions of the detector to be 4 mbar acetone pressure and 745 ± 20 V anode voltage. At these operating conditions, the count rate is improved by a factor of three to what has been reported earlier by Funnemann and Merz. We show that unlike other gas-filled detectors, acetone/ CaF_2 detector works in the proportional region. Its dead time is negligible and addition of multiplier gas like argon worsens its performance. The performance of this detector has been compared with an ethanol/ MgF_2 detector. High count rate, reasonable resolution, negligible dead time, no requirement of multiplier or quench gas, satisfactory stability, and ease of handling make the acetone/ CaF_2 detector an attractive candidate for use in inverse photoemission spectroscopy (IPES). A low-energy electron gun of Stoffel–Johnson type has been fabricated and the beam current profile has been determined as a function of electron kinetic energy. The IPES spectra of polycrystalline Ag and Ta are shown and compared with data in the literature. By fitting the IPES Fermi edge of Ag, we find the overall resolution of the spectrometer to be 0.55 eV and the band-pass of acetone/ CaF_2 detector to be 0.48 eV FWHM.

Keywords: Electron gun, inverse photoemission, photon detector, unoccupied states.

In order to investigate the electronic structure of a solid, it is useful to know the nature of both the occupied and unoccupied states around the Fermi level (E_F). Inverse photoemission spectroscopy (IPES) has

emerged as a powerful technique to study the unoccupied electron states^{1–4}. Gas-filled band-pass Geiger–Müller (GM) type counters are generally used for photon detection in IPES because of their high

efficiency, low cost and simple design^{5–12}. McLean and co-workers have reported various gas/window combinations like ethanol/ MgF_2 , 1-propanol/ MgF_2 , etc. among which ethanol/ MgF_2 was reported^{11,12} to