Accelerator Mass Spectrometer of the Center for Collective Use of the Siberian Branch of the Russian Academy of Sciences

V. V. Parkhomchuk* and S. A. Rastigeev**

Budker Institute of Nuclear Physics, Siberian Branch of the Russian Academy of Sciences,
pr. Akad. Lavrent'eva 11, Novosibirsk, 630090 Russia
*e-mail: V.V.Parkhomchuk@inp.nsk.su
**e-mail: S.A.Rastigeev@inp.nsk.su
Received February 16, 2011

Abstract—The accelerator mass spectrometer developed at the Budker Institute of Nuclear Physics for ^{14}C dating has been installed at the Geochronology of the Cenozoic Era Center for Collective Use. Currently, measurement and sample preparation techniques providing necessary accuracy and sensitivity are under development. Stable performance of the accelerator facility under 1-MV operation with a $^{12}C^{+3}$ ion current above 1 μA at the analyzer exit is achieved, which provides a $^{14}C^{+3}$ ion flux of ~10^4 ion/h from a contemporary sample ($^{14}C/^{12}C \sim 1.2 \times 10^{-12}$). The counting rate from a "dead" sample (MPG graphite) is less than 100 ion/h. The system is flexible enough to be adapted for operation with aluminum and beryllium isotopes. The first radiocarbon concentration measurements in test samples and the system description are presented.

1. INTRODUCTION

The accelerator mass spectrometry (AMS) facility has been developed at the Budker Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences [1]. The AMS method is based on the knocking-out of ions from the sample surface by cesium ions followed by analysis of the former. The study of surfaces by secondary-ionic mass spectrometry (SIMS) is widely used in practice for determining the composition of solids [2]. AMS, in contrast to SIMS, is more sensitive for determining minor impurities in materials (10^{-12}–10^{-15} in comparison with a major element). Such high sensitivity is achieved due to multistage filtering of the ion beam composition in electric and magnetic fields that split the molecular background when ions pass through a special charge-exchange target, and due to the possibility of ion-by-ion counting. In studying samples of unknown composition, a SIMS analysis is usually first performed to determine the main components of a material [3], and only then is an AMS analysis carried out to detect a low concentration of an element to be determined. This is associated with the danger of damaging the supersensitive components of the AMS system and the complex rapid synchronous tuning of filters for passage of other ions.

Supersensitive analysis of ions knocked out from the sample surface finds wide application in such fields as geology, archeology, materials science, and biomedicine. However, AMS analyzers are most commonly used for radiocarbon dating.

2. RADIOCARBON DATING BY ANALYSIS OF IONS KNOCKED OUT FROM A SAMPLE SURFACE

Radiocarbon dating is based on isotope analysis of materials, during which ^{12}C, ^{13}C, and ^{14}C concentrations are measured. The ^{12}C isotope is a major element of carbon material. The natural abundance of the ^{13}C isotope is ~1% of ^{12}C. The fraction of the cosmogenic ^{14}C radioactive isotope is insignificant, 10^{-12} and below. Radiocarbon is mostly produced in the upper atmosphere from nitrogen upon exposure to neutrons released by cosmic rays. Such a state is unstable, and radiocarbon decays into nitrogen with emission of an electron with a half-life of 5730 years. These atmospheric processes result in a ^{14}C isotope balance. However, the radiocarbon concentration in the atmosphere is not constant; it varies in time due to varied cosmic ray intensity and conditions of carbon exchange with the world ocean, the main carbon reservoir. Furthermore, the radiocarbon concentration has varied over recent centuries due to antropogenic activity: deforestation, coal burning, nuclear weapons testing, etc. Numerous scientific studies of the radiocarbon concentration in tree rings and corals (whose age is well known) resulted in the construction of the "calibration curve" [4] describing the radiocarbon concentration in the atmosphere over the last 25000 years. The carbon isotope composition of biosphere elements differs from the atmospheric one (the fractionation effect). For example, only about 98 of 100 ^{13}C isotope atoms (100% for ^{12}C) are transferred to the tree composition during photosynthesis; the fraction of trans-

ferred radiocarbon is smaller than the ^{13}C fraction in the same ratio.

While a biological object "lives," the radiocarbon concentration is controlled by interaction with the biosphere. When an object dies, the radiocarbon content decreases by half every 5730 years. The term "dead" sample is understood as a sample with small radiocarbon content. AMS dating includes ^{12}C and ^{13}C ion beam current measurements and ^{14}C ion-by-ion counting. The radiocarbon concentration is corrected to the fractionation effect by the ratio of ^{12}C and ^{13}C isotopes. Then, using the calibration curve, the age of an object is determined.

3. OPERATING PRINCIPLES OF THE AMS ANALYZER

The sensitivity of mass spectrometry is limited by the background of isobars and molecules with masses close to that of the measured isotope. For example, when measuring the radiocarbon concentration, the number of $^{13}CH^-$ or $^{12}CH_2^-$ molecular ions knocked out from the sample surface exceeds the number of $^{14}C^-$ ions by eight to ten orders of magnitude. Background particles can overcome filters due to the interaction of particles with residual gas and device walls. Among such processes are scattering, charge exchange, energy loss, and molecule splitting. In the AMS method, $^{14}C^-$ ions are accelerated to energies of ~1 MeV followed by ion "stripping" to a charge state of 3+. Since molecular ions in this charge state of 3+ are more unstable and instantaneously split, ions with close masses can be rejected. The masses of the remaining fragments of background molecules differ from the radiocarbon mass by 1 u or more.

The high ion energy at the AMS exit and a small content of background impurities allow the use of Figure 1 shows a diagram of the AMS system. The ions to be analyzed are produced by bombarding the sample surface with cesium ions. Cesium vapor produced by heating of cesium to a temperature of ~200°C, through a tube, reaches a tantalum ionizer heated to ~1000°C. On the hot surface of the latter, positive cesium ions are generated, which are accelerated and focused on the cathode with the sample under study. Negative ions knocked out from the sample surface are accelerated to the ionizer at the same potential and, having passed the ionizer aperture, are accelerated by the ground potential to an injection energy of 25 kV. Then, the ions are turned by 90° in a magnetic field and are accelerated vertically upwards in the first accelerator tube to the positive potential of the high-voltage terminal (1 MV). Ions are stripped to a positive charge in the target in magnesium vapor, are turned by 180° in an electric field, and are then accelerated downwards in the second latter accelerator tube to the ground potential. Accelerated ions are turned by 90° in a magnetic field and arrive horizontally at the time-of-flight particle detector.
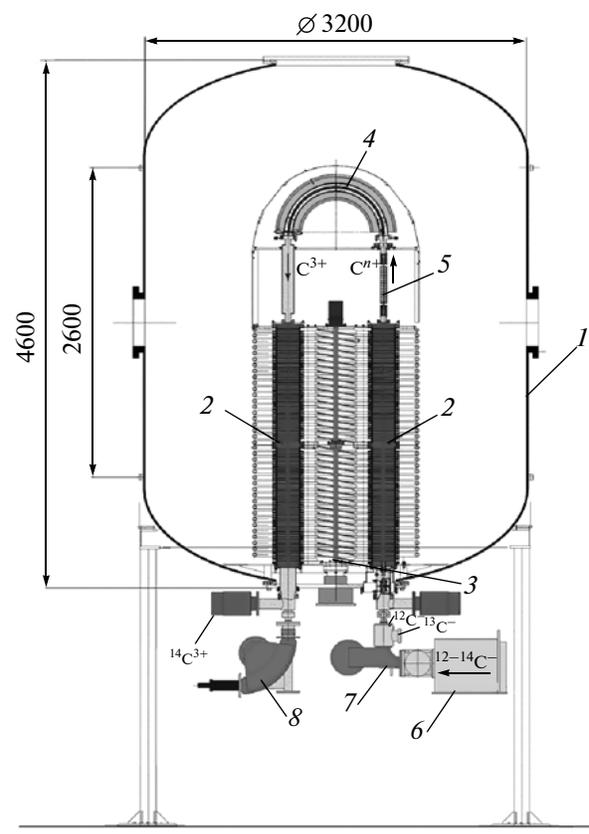

Fig. 1. Accelerator mass spectrometer: (*1*) tank for insulating gas, (*2*) accelerator tube, (*3*) cascade rectifier, (*4*) electrostatic filter (deflector), (*5*) magnesium-vapor target, (*6*) ion source, (*7*) and (*8*) magnetic filters.

4. FEATURES OF THE DEVELOPED AMS ANALYZER

Like most existing AMS analyzers, the system of the Budker Institute is based on a tandem electrostatic accelerator. The sample under study is under a low potential, outside the accelerator tank, which allows easy change of samples. Moreover, the use of negative ions in the first selection stage makes it possible to significantly lower the isobaric background in some cases. For example, it is known that negative ^{14}N nitrogen ions are unstable. Nevertheless, nitrogen appears in the system as molecule fragments which can have a negative charge and can be involved in acceleration to the high-voltage terminal. However, in the project under consideration, the emphasis is on the idea that the background particle flux can be significantly lowered using an energy filter in the high-voltage terminal (electrostatic turn by 180°). In this case, the background of ^{14}N ions (whose mass differs slightly from the ^{14}C mass) can be totally suppressed by this filter, since nitrogen is formed by fragments of molecules split before the electrostatic turn during charge exchange, i.e., has a lower energy than radiocarbon ions. If nitrogen ions were not filtered after the first
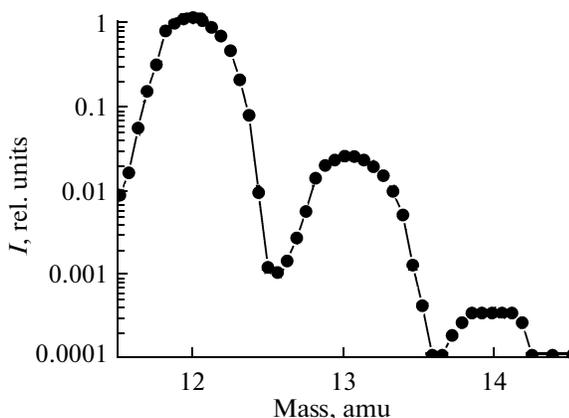
Fig. 2. Mass spectrum of negative ions knocked out from the graphite surface.

acceleration stage, in the second acceleration stage, their energy can become equal to the radiocarbon ion energy [5], which will make it almost impossible to separate them in electromagnetic fields.

Another essential feature of the project under consideration is the use of a magnesium vapor target for ion charge exchange [6]. The ion charge exchange region is strongly localized, since magnesium vapor can be reflected only from a hot surface. In the case of gas targets, a gas fraction inevitably appears in the electric field region of the tandem accelerator, which results in charge exchange of an ion fraction in the electric field, hence, an energy spread in the ion beams, which allows the ion background to overcome filters. Cold (room temperature) surfaces of the vacuum chamber have a high absorbance of magnesium molecules, comparable to that of cryogenic pumps. For example, a vacuum tube 300 mm long and 50 mm in diameter will be characterized by a pumping rate of 10000 l/s for magnesium vapor, which is difficult to achieve using turbomolecular pumps for gas targets.

5. EXPERIMENTAL RESULTS

Both atomic and molecular ions are knocked out from the sample surface. Figure 2 shows the typical mass spectrum of graphite ions in the range of carbon isotope masses, measured at the exit of the magnet followed by the ion source. We can see that the content of 13-u ions is slightly higher than 2%. Since the natural abundance of the ^{13}C isotope is ~1%, it is clear that the contribution of $^{12}CH^-$ molecular ions to the measured 13-u peak is comparable to that of $^{13}C^-$ ions. The difference between the masses of ^{13}C and ^{12}CH is ~10^{-3}. Since the contributions of atomic and molecular ions to the measured 13-u peak are comparable, they can be separated and measured using conventional mass spectrometry methods with sufficient mass resolution. However, if the molecular peak is much larger the atomic one, separation is possible only using AMS methods with total splitting of molecules. Figure 2

shows that the 14-u peak is almost completely represented by the molecular background, since the natural content of the ^{14}C isotope in a contemporary sample is ~10^{-12}.

Ions of various charge states are produced when the ion beam passes through the target. If the latter is sufficiently thick, the charge distribution is independent of the initial ion charge, but is controlled by the ion energy. The higher the energy, the larger the average ion charge at the target exit. To provide a sufficient number of ions of charge 3+, the electrostatic accelerator voltage was increased to 1 MV. The fraction of triply charged ions measured at the AMS analyzer exit was ~10% of negative ions knocked out from the sample surface. The ^{12}C ion beam intensity was measured by a Faraday cup. $^{14}C^{3+}$ ion-by-ion counting was performed by a time-of-flight detector. The latter allows not only counting of the number of arrived ions, but also measurement of times of flight through two rectilinear sections for each particle [7]. Thus, additional selection of particles by their velocity is performed, which makes it possible to reject cosmic ray particles arriving at the detector. The latter consists of three sequentially arranged sensors fixing the time point of particle flight. The notations ToF 1-2 and ToF 1-3 used in what follows correspond to times of flight of ions between the first and second and first and third sensors, respectively. The time of flight is given in channels of digitizing electronics; each channel is equal to 7×10^{-11} s. Figure 3 shows the two-dimensional time-of-flight spectrum for "living" (a) and "dead" (b) carbon. The former sample was prepared by pressing of carbon fibers; the latter is MPG-type graphite. In Fig. 3a, we can clearly see the peak of radiocarbon to which the AMS analyzer is tuned. We can also see a small peak of background ^{13}C ions (the center of the peak is at the 508th and 820th channels on the ToF 1-2 and ToF 1-3 axes, respectively) reached the last detector. It is interesting that the number of background ^{13}C ions for graphite (Fig. 3b) is significantly smaller. This is probably caused by the fact that the hydrogen content in graphite is much lower than in carbon fibers pressed in air, and the transmitted background ^{13}C ions are fragments of $^{13}CH^-$ molecules. However, in any case, we can see good separation between the radiocarbon peak and the closest-mass element.

A multiposition (23 samples) source of negative ions is installed at the AMS facility. Remote sample changes are performed by a step motor which rotates a sample drum with a discreteness of 1/51 200 of a drum revolution. The computer control system positions chosen samples according to a set cycle. For each sample, ^{14}C ion-by-ion counting and ^{12}C ion current measurement are performed. Figure 4 shows the result of measurements of all samples placed in the drum. The vertical axis is the number of ^{14}C ions detected per hour, normalized to 1 μA of $^{14}C^{3+}$ ions. Radiocarbon measurements were carried out for 800 s for each sam-
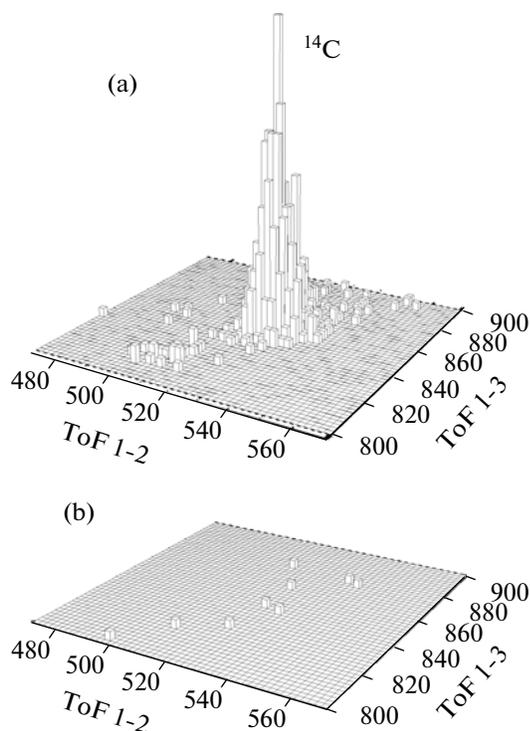
Fig. 3. Time-of-flight spectrum of ions at the AMS analyzer exit for (a) carbon fabric and (b) graphite samples.

Fig. 4. Radiocarbon concentration in tested samples.

ple; the root-mean-square statistical acquisition error is also shown in the figure. Sample nos. 1, 3, and 10 were made of carbon fabric produced from contemporary cellulose; samples nos. 2 and 4, of MPG graphite. Other samples were prepared as follows. A sample was burned in vacuum with added oxygen, produced carbon dioxide was deposited on a catalyst with added hydrogen, and the obtained mixture was pressed. This procedure allows preparation of samples with a high carbon concentration from materials with low carbon content. Samples nos. 5–9, 17–23 were prepared from graphite or "dead" CO_2. They were used to work out the technology for preparing samples with minimum contemporary carbon impurity. Sample no. 20 was made of petrified wood whose age was estimated as 30 000 years using a setup determining radiocarbon content by decay. Sample no. 11 was prepared from contemporary citric acid; samples 12–16 were made of 1977 oxalic acid using different technologies. We can see that the contemporary carbon contents in samples 1, 3, 10, 11 are in good agreement; increased signals from samples 12–16 are caused by the total ^{14}C carbon increase due to nuclear tests. The ^{14}C content is less than 1% of the contemporary sample; additional ^{14}C in background samples is minimum for no. 18. This sample was made of imported preparations for CO_2 purification and graphitization. The use of high-purity grade preparations is probably inevitable for such studies, in spite of their high cost. The radiocar-
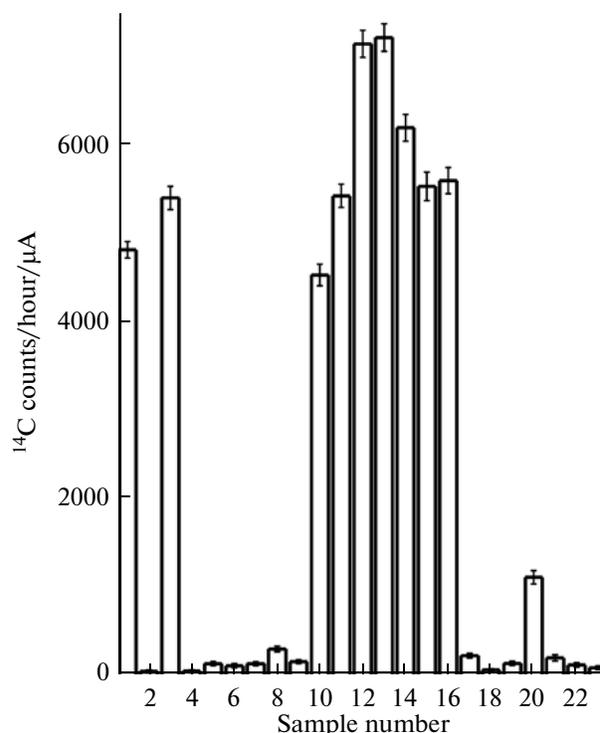
bon content in sample 20 is ~22% of contemporary present-day samples, which corresponds to an age of 14 200 ± 700 years. The measured graphite age is 42 000 years (the ^{14}C concentration is 1% of contemporary samples) and approaches the limit of reliable data of modern AMSs.

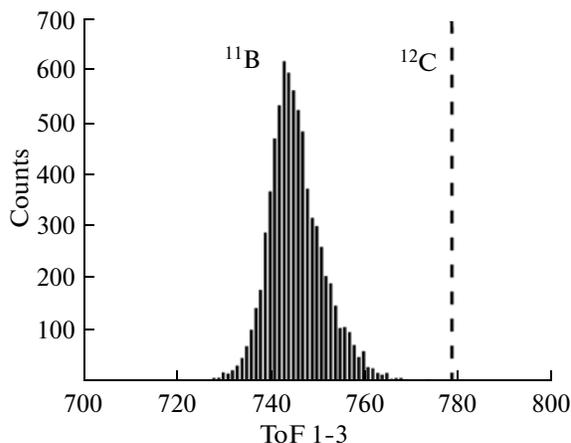Graphite consisting mostly of carbon contains minor impurities of other elements. Figure 5 shows

Fig. 5. Time-of-flight spectrum of ions at the exit of the AMS analyzer adjusted to ^{11}B ion transmission for measuring minor boron impurities in graphite.

the time-of-flight spectrum at the AMS analyzer exit after retuning the system to ^{11}B ion transmission. The boron concentration in graphite is 10^{-6} in comparison with carbon. This concentration exceeds the limit detected by the AMS analyzer by many orders of magnitude; therefore, there are no ions of mass 12 u corresponding to the major graphite component in the spectrum.

6. CONCLUSIONS

The capabilities of the described AMS analyzer for measuring ultralow isotope concentrations are demonstrated. The measured radiocarbon concentration in graphite is 10^{-14} in comparison with carbon of mass 12 u (1% of the ^{14}C concentration in the atmosphere). An analysis of a set of graphitized samples shows that achieving a low background close to the graphite background requires high-quality materials and special clean conditions of sample preparation. It was shown that the ^{14}C concentration in carbon fabrics is close to the expected value for contemporary carbon in cellulose. Such preparations can be good markers for calibrating samples in addition to reference samples requiring graphitization. Their high stability and unnecessary chemical treatment (which could change the ^{14}C content) will make it possible to reliably monitor the transport through the AMS analyzer to provide reproducibily of results of analysis.

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