

# RADIOCARBON ANALYSIS OF DIFFERENT SAMPLES AT BINP AMS

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## Abstract

The accelerator mass spectrometer (AMS) created at BINP is used for biomedical, archaeological and other applications. Present status and experimental results are described.

## INTRODUCTION

The accelerator mass spectrometry is an ultra-sensitive method of isotopic analysis for archaeology, geology, biomedical science and other fields. It's based on measurements of the ratio between isotopes. The ratio between isotopes in sample can be less than  $10^{-15}$ . So, the counting methods are used for detection of such low radiocarbon concentration [1-5]. The AMS is based on the electrostatic tandem accelerator. The AMS system consists of the ion source, low energy channel, tandem accelerator and high-energy channel [6-8]. The low energy beam line is used for initial isotopes selection. The tandem accelerator is applied for rejection of the molecular ions and of course for obtaining necessary beam energy for radioisotopes detector. The high-energy beam line is used for the subsequent ions selection and for radioisotopes detection.

. The most distinguishing feature of our AMS machine is the use of additional electrostatic separator of ion beam, located inside the terminal. In this configuration of the AMS, the ions background is significantly reduced by the energy filter in the high voltage terminal. Interfering isobaric molecules are destroyed by collisions in the stripper into the terminal and are selected immediately after the stripping process. It is important to decrease the background from molecular fragments before the second stage of acceleration [9-10], because the energy of fragments is always less than the ion energy (at this moment). The next important distinguishing feature is magnesium vapours stripper [11] instead of the gas stripper. The gas flow into the accelerator tubes leads to big energy spread in the beam thus limiting the sensitivity and accuracy of spectrometer. The molecular destruction and ion recharging by magnesium are localized into the hot tube of the stripper. Moreover, the moment of time for ion detection can be registered with  $16 \mu\text{s}$  channel width by TOF detector [12,13]. This data is used for calculation of number of detected ions per unit time, allowing filtering the background ions from electrical breakdowns.

## AMS ANALYSIS ALGORITHM

During the measurements of user samples, the injection energy of radiocarbon beam was about 25 keV. The terminal voltage of tandem accelerator was 1 MV. The  $180^\circ$  electrostatic bend was set to transmit the ions with charge state  $3+$ . The magnesium vapors stripper was heated for obtaining the equilibrium charge state distribution, but not more. The vacuum in the beam line was about  $10^{-6}$  Torr.

The 20 graphitized samples are setted in the ion source sample wheel to measure the concentration of radiocarbon. Furthermore, the 3 control sample with a known concentration of radiocarbon is setted in ion source sample wheel for control and normalization of the measurement samples. Typically, this sample are two carbon wire with a carbon concentration on the natural content of modern plants and one sample of graphite MPG with radiocarbon concentration at  $2 \cdot 10^{-3}$  compared to modern plants. It should be noted that the control samples did not require the procedure of graphitization and setted in the sample wheel in natural form.

When measuring the concentration of radiocarbon in the samples, the switching algorithm is used. The isotope  $^{14}\text{C}$  is detected by TOF telescope and  $^{13}\text{C}$  currents are measured at the exit of AMS. For switching algorithm the high voltage of ion source is changed. The energy of the cesium ions remains constant. The electrostatic lens and correctors at the exit of the ion source are changed for each isotope. Thus, the passage of isotopes is carried out through a first dipole magnet, without changing the magnetic field. The magnetic field in high energy magnet is not changed to, because the radial aperture is wide enough for passing radiocarbon ions to TOF detector and  $^{13}\text{C}$  ions to shifted FC.

The cycle of AMS-analysis of samples is represented as follows. For each sample, the  $^{14}\text{C}$  ions are counted four times (10 seconds each) and twice the  $^{13}\text{C}$  currents are measured for each 10 seconds counting. After that, the samples wheel is turned to the next sample for process repetition. Measuring of whole graphitized sample wheel (20 samples) takes about 15 minutes. For a set of statistics the wheel are moving to the second turn, third, etc. Typically, the measurement will take approximately 5 hours, with a statistical error of measurement for modern samples less than 1%. The process of isotope measuring and sample changing (wheel rotation) is fully automated.

## SAMPLES FOR AMS ANALYSIS

For AMS analysis, all samples must be converted to so-called "graphite". For these purposes, a sample is combusted in vacuum. Then the carbon from formed CO<sub>2</sub> gas catalytically deposited on iron powder. The Fe-C mixture is pressed in aluminum sample holder (cathode for ion source) for AMS analysis.

Now at BINP AMS used two types of sample holders: with inner diameter of 2 mm (for about 3 mg of carbon sample) and with inner diameter of 1 mm (for 1 mg or less of carbon sample). The 1 mm and 3 mm samples can be installed in the sample wheel together. The sputtering by Cs beam region of the sample is about 0.5 mm in diameter. The new alignment system was manufactured for the Cs beam hitting in the center of the 1 mm target.

Now at BINP AMS used graphitized samples from NGU and LAE SB RAS chemists and a number of samples graphitized at IG RAS. Samples are produced from a variety of natural materials: bone, charcoal, wood etc.

The quality of sample preparation is crucial for formation of negative carbon ions from ion source, because sufficiently good thermal conductivity of samples is needed. The sputtered carbon atoms capture electrons from the cesium, which was accumulated on the surface of the sample. If thermal conductivity of samples is low, the cesium atoms are evaporated from sample surface. Typically, the maximum current is obtained from graphite without sample preparation. The currents from graphitized natural samples are in the range from graphite currents level to much smaller level.

Contamination during sample preparation can significantly affect to the dating results. The "dead" carbon pollution (for example, the carbon from technical oil) increases the age of dating objects. The "modern" carbon pollution (for example, the carbon from atmospheric CO<sub>2</sub>) decreases the age of dating objects.

## RADIOCARBON MEASUREMENTS

Over the last year, more than 1000 samples were analyzed at BINP AMS. The typical carbon beam currents from samples during samples wheel rotation are present at the Fig. 1 (a). As seen, the beam current of sample from sample position 14 (sp14) is so much smaller than the other. The vacuum is worse, when the sp14 sample is sprayed by cesium beam Fig. 1 (b). The vacuum remains good enough and does not affect to the beam transmission efficiency. During the measurement, the gassing from such sample is reduced, but the carbon current is not increased significantly. The mean currents for the time of AMS analysis are present at the Fig. 1 (c). Typically, the currents from samples can differ twice. The carbon beam current ratio from the different samples can be changing during the measurement. This depends on the special features of graphitization for each sample. However, beam current from some samples can be very small (as from sp14 sample). Significant number of the samples with a small current is contaminated by external carbon

during graphitization. The radiocarbon dating of samples with small current is not reliable and usually necessary graphitize additional sample. Moreover, the statistical error of measurements for such samples is significantly greater than for the other samples.

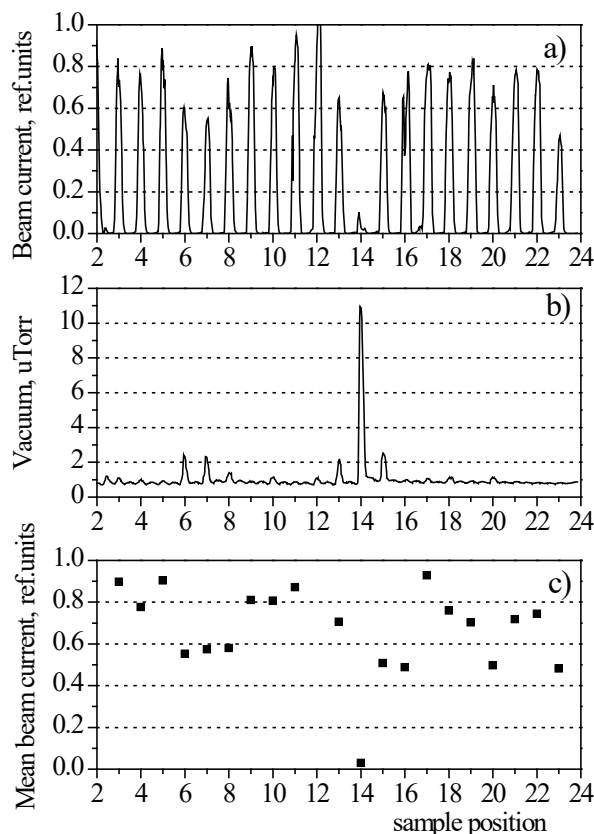


Figure 1: The carbon beam current a), mean current c) and the residual gas pressure b) for samples.

The kinds of pollution can differ in the graphitized samples. The oxygen current from samples during sample wheel rotation are present at the Fig. 2. The AMS was tuned to the passage of oxygen beam. The sample in position 2 is a graphite MPG (without sample preparation), the samples in positions 1, 12 are carbon wires (without sample preparation), the other samples - graphitized natural objects. As seen, the oxygen content in graphitized samples is significantly higher than in technical graphite MPG. Many other chemical elements can be present even in "clean" samples. For example, the boron concentration normalized to the carbon is about  $10^{-6}$  in graphite MPG without sample preparation, the lithium concentration - about  $10^{-9}$ . But, if the radiocarbon selection in AMS is good enough, it is not a problem for radiocarbon dating. The light atoms can pass the injection magnet as part of the molecule 14 a.m.u. mass as if radiocarbon ions. Such atoms are separated from radiocarbon beam by energy filter in the high voltage terminal at BINP AMS.

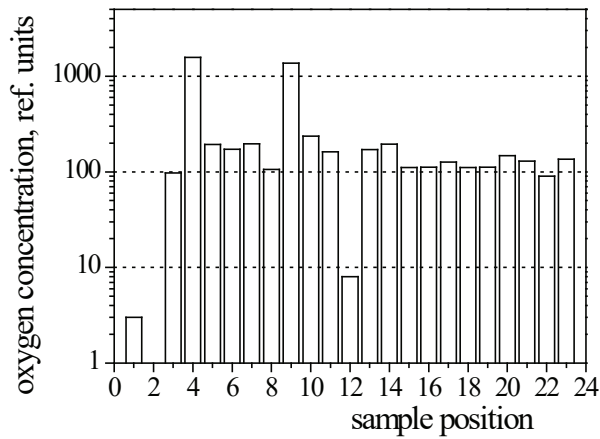


Figure 2: The oxygen beam currents from the samples.

The isotope ratio may differ significantly before and after graphitization (fractionation effect). The measured radiocarbon concentrations in graphitized samples of OXII (oxalic acid natural standard) are present at the Fig. 3. The data are normalized to the radiocarbon concentration in carbon wire (without sample preparation). As seen in Fig. 3, the radiocarbon concentration in the samples is less for sample preparation by NSU than by IG RAN. This should be considered when calculating the radiocarbon age of the samples. So, the concentration of radiocarbon in the unknown samples is normalized to the radiocarbon concentration in standards prepared by the same laboratory. This is necessary for the correct dating of the samples.

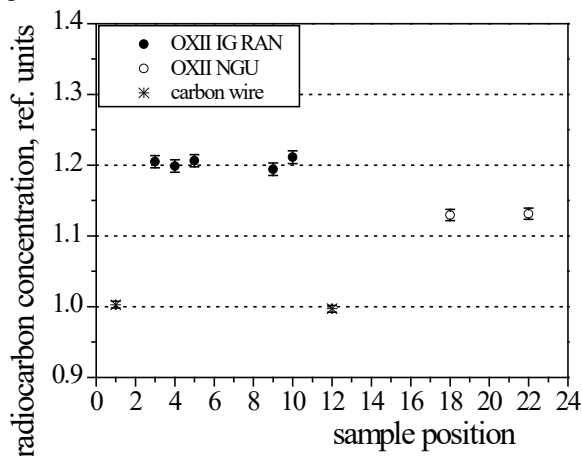


Figure 3: The radiocarbon standards from different laboratories.

Atmospheric carbon is permeated into the samples during graphitization. Samples used for radiocarbon dating must be handled carefully to avoid contamination. The contamination level in the samples during the sample preparation procedure is estimated by the radiocarbon content in graphite after combustion and graphitization (the radiocarbon concentration in graphite is insignificant before this procedure). The concentration of radiocarbon

in the prepared graphite depending on the weight of the sample is presented in Fig.4.

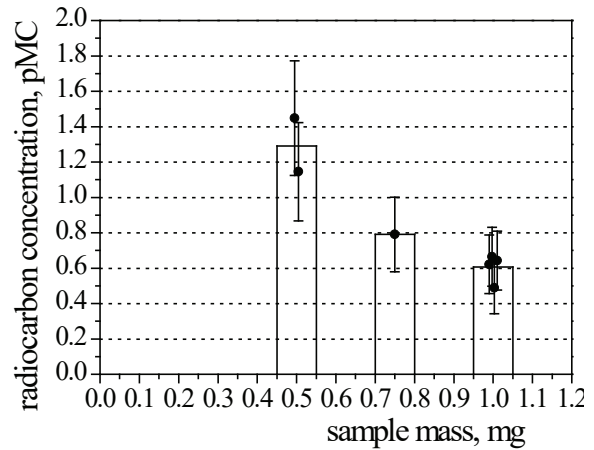


Figure 4: The concentration of radiocarbon in the prepared graphite as a function of sample mass.

The results are reported using the unit pMC (percent modern carbon). The radiocarbon concentration in atmospheric CO<sub>2</sub> is about 100 pMC. As seen from Fig. 4, the level of sample contamination decreases with increasing of sample mass. Moreover, the contamination level depends on the sample type and the technology being used for sample graphitization. It is different for different sample preparation laboratories. Typically, the contamination level is about 1 pMC. Note that the radiocarbon concentration of graphite MPG without sample preparation procedure is about 0.2 pMC.

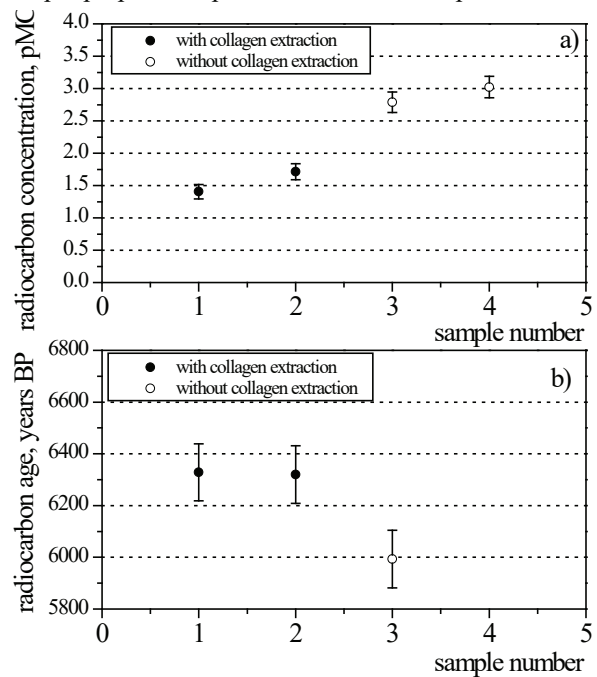


Figure 5: The radiocarbon concentrations in old rhinoceros with and without collagen extraction (a), the radiocarbon age of young mammoth with and without collagen extraction (b).

Usually, the specific functions of natural samples are used for graphitization. For example, collagen is used for the bone samples or cellulose - for wood samples. This reduces the influence of natural pollution on the radiocarbon dating. The results of AMS measurements of old rhinoceros with and without collagen extraction are presented in Fig.5 (a). As seen, the radiocarbon concentration in samples is smaller with collagen extraction than without. This is because the rhinoceros bone is contaminated by modern carbon. Similarly, for a young mammoth: the measured mammoth age is older with collagen extraction than without. As is known, the radiocarbon dating of bone is more correct with collagen extraction from natural samples than without.

As an example of AMS-analysis, the data from geological samples - lake Sargul sediments, depending on the depth from surface level (samples of Krivonogov S.K., IGM SB RAS), presented in Fig. 6. Such analyzes are necessary to obtain a timescale for lake sediments. Such results are quite revealing, since in the absence of mixings deposits should be observed dependence - the deeper the ancient.

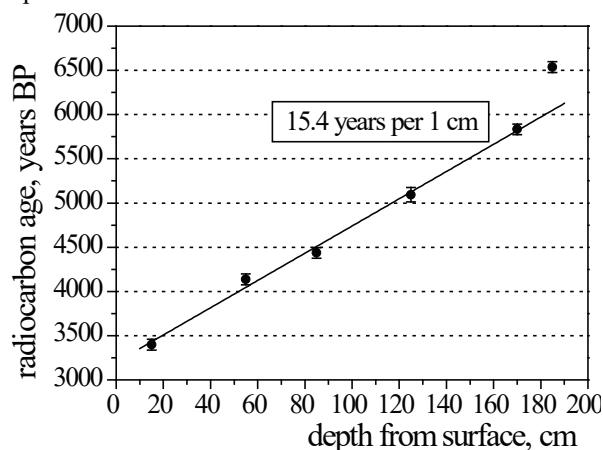


Figure 6: The radiocarbon age of lake sediments, depending on the depth from surface level.

## SUMMARY

The BINB AMS is used for radiocarbon analysis of graphitized natural samples. The algorithm of the AMS analysis was described. Currently, the samples measured by BINB AMS are prepared from some independent chemical laboratories. The natural and chemical contamination of samples can be detected at BINB AMS.

## REFERENCES

- [1] S.A. Rastigeev et al, "Operation and development of the BINP AMS facility ", Proceedings of RuPAC-2014, Obninsk, Russia, 2014, p. 134.
- [2] S.A. Rastigeev et al, Acceleration Mass Spectrometer of the Budker Institute of Nuclear Physics for Biomedical Applications // Physics of Particles and Nuclei Letters, 2014, V. 11, № 5, p. 642

- [3] S.A. Rastigeev et al, "First radiocarbon measurements at BINP AMS", Proceedings of RuPAC-2010, Protvino, Russia, 2010, p. 309.
- [4] S.A. Rastigeev et al, Accelerator mass spectrometer SB RAS // Problems of Atomic Science and Technology/ Series "Nuclear Physics Investigation". 2013, №6(88), p. 16.
- [5] Parkhomchuk, V. V., Rastigeev S.A., Accelerator mass spectrometer of the center for collective use of the Siberian Branch of the Russian Academy of Sciences // Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques, 2011, V. 5, Issue: 6, p.1068
- [6] N.I. Alinovskii et al, Accelerator mass spectrometer for the Siberian Branch of the Russian Academy of Sciences. // Technical Physics, 2009, Vol. 54, No 9, p 1350.
- [7] S.A. Rastigeev et al, Development of the BINP AMS complecs at CCU SB RAS. // Problems of Atomic Science and Technology/ Series "Nuclear Physics Investigation". 2012, №3(79), p. 188.
- [8] S.A. Rastigeev et al, Recent results in accelerator mass spectrometer construction at BINP. // Problems of Atomic Science and Technology/ Series "Nuclear Physics Investigation". 2008, №5, p. 8.
- [9] Parkhomchuk, V. V., Rastigeev S.A., Ion selection in accelerator mass spectrometer at the Budker institute of nuclear physics // Physics of Particles and Nuclei Letters, 2012, V. 9, Issue 4-5, p. 406
- [10] V.V. Parkhomchuk and S.A. Rastigeev, Analysis of the ion background in an acceleration mass spectrometer of the Siberian Division of the Russian Academy of Sciences. // Technical Physics, 2009, Vol. 54, No. 10, p 1529.
- [11] V.F. Klyuev, V. V. Parkhomchuk, S.A. Rastigeev, A magnesium vapor charge-exchange target for an accelerator mass spectrometer. // Instruments and Experimental Techniques, 2009, Vol. 52, No. 2, p. 245.
- [12] N.I. Alinovskii et al, A time-of-flight detector of low-energy ions for an accelerating mass-spectrometer. // Experimental Techniques, 2009, Vol. 52, No. 2, p. 234.
- [13] V. V. Parkhomchuk et al, Thin-film detector for ion registration in accelerator mass spectrometers // Physics of Particles and Nuclei Letters, 2012, V. 9, Issue 4-5, p. 448