

# IMPROVEMENTS AND APPLICATIONS OF AMS RADIOCARBON MEASUREMENT AT PEKING UNIVERSITY

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**ABSTRACT.** AMS radiocarbon measurements were started at Peking University in 1992 with a modified HICONEX 834 ion source. Some archaeological samples were measured at a sensitivity of  $10^{-14}$  with *ca.* 1.7% precision for modern samples. We have made many improvements in our first two years of operation: a high-intensity Cs sputtering ion source was installed; the graphite sample preparation technique was investigated; and the system stability has been improved. The blank sample background is currently *ca.* 0.006 MC and a precision within 1% can be reached for modern samples. Geological, archaeological, environmental and biomedical samples can be measured routinely. We present some typical applications.

## INTRODUCTION

To fulfill the requirements of measuring many  $^{14}\text{C}$  samples in China, the Peking University Accelerator Mass Spectrometer (PKUAMS) was constructed from 1990–1992 (Chen *et al.* 1990, 1992). Figure 1 shows its schematic layout. The first batch of  $^{14}\text{C}$  samples were measured with a modified reflection-type HICONEX 834 ion source in 1992 (Chen *et al.* 1993). A precision of 1.7% for 2 ka old samples and a sensitivity of  $10^{-14}$  were reached. Since then we have made efforts to improve the performance of the  $^{14}\text{C}$  measurements. Since May 1993, PKUAMS began routine  $^{14}\text{C}$  measurements with a high-intensity sputter ion source (Chen *et al.* 1994). We further investigated various problems of impaired performance. As a result of the first phase of improvement, the sensitivity of  $^{14}\text{C}$  measurement became an order of magnitude higher than it was before and a precision better than 1% for modern samples was achieved. The throughput was raised to *ca.* 12 samples of unknown age per day. Since May 1993, applications in the fields of geoscience, archaeology, environmental science and biomedical science have progressed. Further improvements are also under consideration.

## METHOD

Graphite sample preparation of PKUAMS is based on direct  $\text{CO}_2$  catalytic reduction on iron powder, as described by Vogel, Nelson and Southon (1987). Figure 2 outlines the preparation system. Reaction tube  $A_1$  is used to produce  $\text{CO}_2$  by heating organic materials with  $\text{CuO}$  or acidolysis of carbonate with phosphoric acid. Liquid nitrogen traps  $C_1$  and  $C_3$  and dry ice trap  $C_2$  are used to purify the  $\text{CO}_2$ . Iron powder is put in a small copper disk, which is supported by a tungsten wire in reaction tube  $A_2$ .  $A_2$  is filled with the purified  $\text{CO}_2$ , which is then mixed with  $\text{H}_2$  at a volume ratio of 1:3. When the iron powder is oven heated to *ca.*  $540^\circ\text{C}$ , the  $\text{CO}_2$  converts to graphite and the water produced during the reaction is frozen in dry ice trap  $C_4$ . The reaction takes *ca.* 2–3 h.

We studied possible improvements in sample preparation to gain measuring potential. Our experience indicates that some steps are essential for achieving low background. Before filling it with sample  $\text{CO}_2$ , we pump and heat the reactor  $A_2$  to remove the absorbed gas, then fill it with 0.5 atm  $\text{H}_2$ , heat  $A_2$  and cool  $C_4$  to eliminate any remaining  $\text{CO}_2$  in the iron powder. Remnant hydrogen absorbed in the graphite is harmful to our measurements. It produces molecular ions  $^{13}\text{CH}^-$  and  $^{12}\text{CH}_2^-$  in the ion source, which are dissociated by a stripping process and generate a continuum.

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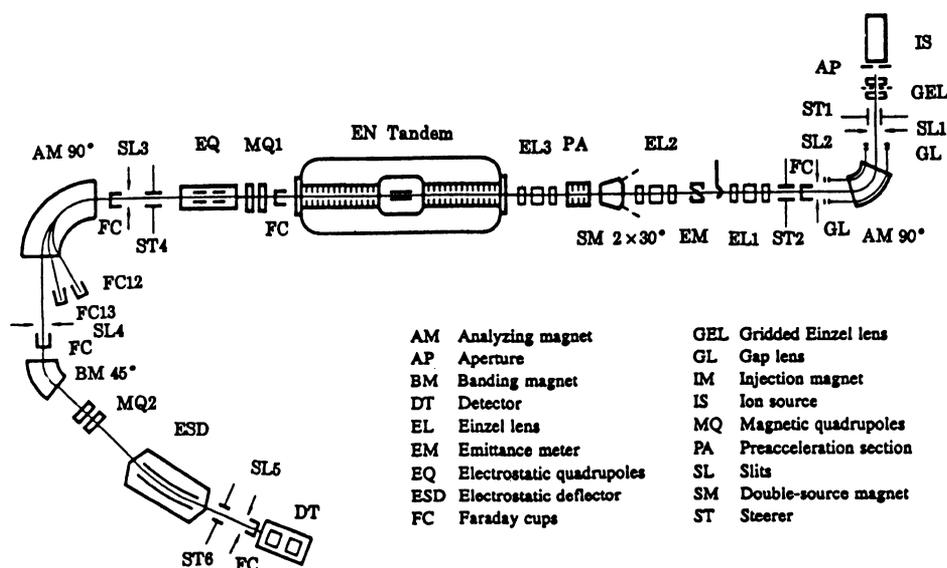


Fig. 1. Schematic layout of PKUAMS

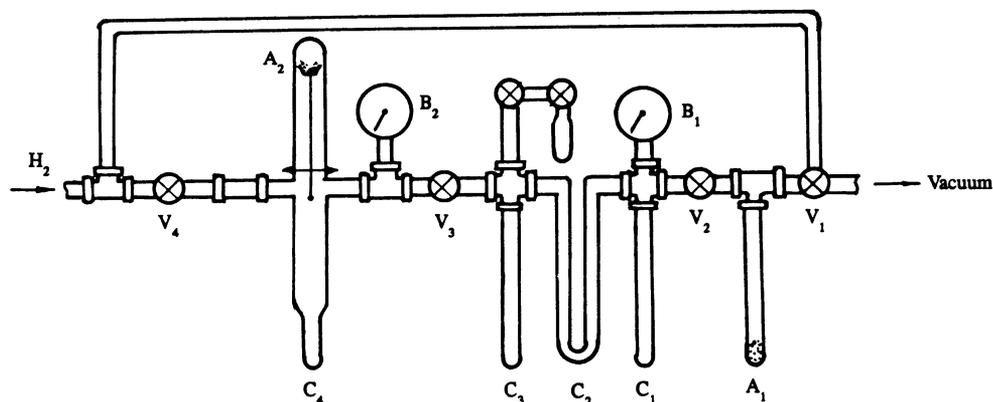


Fig. 2. Graphite sample preparation system: A=reaction tube; B=pressure meter; C=cold trap; V=valve

This is one of the main sources of measurement background. Therefore, we must pump the system for a sufficient period of time after the reduction reaction to evacuate the residual hydrogen from A<sub>2</sub>. The memory effect of the sample preparation system must also be considered. Experiments show that the anthracite blank sample prepared immediately following a contemporary sample usually yields a higher <sup>14</sup>C concentration. In this case, it is helpful to clean the system with “dead” CO<sub>2</sub> before preparing an “old” sample. Different carbonaceous fractions are usually extracted and dated separately for samples of complex composition, such as sediments and soil. This procedure gives better reliability.

The dedicated ion source developed at the Shanghai Institute of Nuclear Research (Si *et al.* 1992) has a spherical ionizer. Up to 150 μA of C<sup>-</sup> beam can be extracted from a graphite target with an

Fe:C ratio of *ca.* 3:1. The throughput of PKUAMS has been improved with the high-intensity source.

The sample wheel in the ion source has 20 positions and can be rotated using a stepping motor. There is a valve between the wheel and sputtering area. The sample holder is fixed on a cartridge, which can be inserted on the sample wheel and pushed forward to the point of cesium bombardment by a motor-driven rod. The initial design of the sample-changing feature was imperfect both in mechanism and in the electronic control. At times the wheel would stop at a wrong position after rotation or the cartridge might drop from the end of rod when it was being withdrawn.

To improve reliability, the mechanism was partly redesigned and a new control system with an interface to a console computer is being developed. Reliability improved when we ran the ion source at a lower level with reduced ionizer heating power, although the current also dropped under this condition. We usually keep the extracted C<sup>-</sup> beam at 30–50  $\mu$ A for routine measurements and 12 unknown samples can be measured per day. We hope to increase throughput after improvements of the ion source are completed.

Measurement background is related to the vacuum conditions in the acceleration tube and high-energy spectrometer due to charge-changing processes (Purser and Litherland 1990). The vacuum of PKUAMS has been improved since the first batch of <sup>14</sup>C samples were measured. A new gas stripper with recirculation will be constructed in near future. After the differential pump is installed in the terminal of EN tandem, we will be able to maintain a good vacuum in the acceleration tube.

We have also improved the stability of the power supply. Long-term stability of terminal voltage is improved to better than  $\pm 1.0$  kV when the terminal voltage is 3 MV for <sup>14</sup>C measurements. We obtained a precision better than 1% for modern samples. Blank sample background is usually *ca.* 0.006 pMC. We successfully measured a 0.4 mg C sample to *ca.* 15 ka BP. The narrow channel of the gas stripper now limits the flat-topped transmission (Hedges 1987) for the components in the low-energy transport system. The goal of the second phase of improvement is to reach a precision of 0.5% for modern samples by using the new recirculation gas stripper and a grid lens at the entrance of the acceleration tube.

## APPLICATIONS

From May 1993 to June 1994, we measured 520 <sup>14</sup>C samples, including 107 standards, 44 blanks, 46 samples of known age, 38 samples for testing the apparatus and 285 samples of unknown age. Among these 137 samples are for geoscience, 78 for archaeology, 23 for environmental science and 47 for biomedical science. Some typical applications follow.

### Geoscience

To study changing paleoclimates in arid and semi-arid areas of northern China, we are collaborating with the scientists of Geological Institute, Academia Sinica in high-resolution dating of a loess profile at Weinan, Shaanxi Province. An age of 10,300 BP has been attributed to the boundary between the base of the paleosol S<sub>0</sub> and the first loess layer L<sub>1</sub> of the profile, which could indicate the beginning of the Holocene in the areas under investigation.

In southern China, karst deposits can be used to obtain paleoclimatic information. Collaborating with the Institute of Karst Geology, we studied the changing paleoenvironments in high resolution with a stalagmite of 1.2-m height taken from Panlongdong (Bent Dragon Cave), Guilin. AMS <sup>14</sup>C dating with microstratification sampling shows that the deposition rate varied from 0.012–2.8 mm

yr<sup>-1</sup> during the past 30 ka and the  $\delta^{18}\text{O}$  value agrees well with the deposition rate. The highest  $\delta^{18}\text{O}$  value occurred from 12–32 ka BP, representing the lowest temperature in the last glacial epoch. The climate during the Holocene was generally damp and warm, but there was a short cold period from 10–11 ka BP, which may indicate the Younger Dryas (YD) in this area. The resolution of AMS <sup>14</sup>C dating of the stalagmite is 100 yr for the warm, humid period and 500 yr for the dry, cold period.

### Archaeology

We have dated many interesting archaeological samples; for example, a charred wheat seed from Gansu Province, western China dated to 4230 BP. This is the earliest date for wheat cultivation in China, although rice and millet cultivation started much earlier, at *ca.* 7700 BP. Our measurement indicates that wheat might have been imported from the West at that time. We also dated soot separated from the surface of a pot, which yielded ages appropriate to the pottery itself and its associated culture.

Other archaeological samples came from Bailiandong (White Lotus Cave) and Miaoyan (Temple Rock) sites, which contain rich cultural remains from the Paleolithic to the Neolithic. The study yielded information on the transition from the Paleolithic to the Neolithic in South China (Yuan *et al.* 1995).

### Environmental Science

Collaborating with the Center of Environmental Science at Peking University, we identified the sources of atmospheric aerosols (Shao 1994). We measured carbonaceous species of samples from the suburbs (Zhongguancun) and urban districts (Dongdan) of Beijing, as well as from Zhuzhou, Hunan Province and Qingdao, Shandong Province during both cold (when heating is required) and warm (when no heating is required) seasons. The results show that the carbonaceous species in atmospheric aerosols have different source characteristics from trace element species. AMS <sup>14</sup>C measurements of surface soil samples show that carbonaceous species in the soil of various regions contain considerable amounts of carbon from fossil-fuel burning. For carbonaceous aerosols from Beijing, Hunan and Qingdao, the relative contribution of fossil fuel is nearly 2/3, and with increased human activity, the fossil fuel contribution is greater. Taking Dongdan region as an example, AMS measurements show that >95% of carbonaceous aerosols come from fossil-fuel burning during winter when homes are heated. Trace elements and carbonaceous species have similar mass percentage in atmospheric particulate matter, but their emission sources differ significantly. Multivariate analysis shows that the predominant particle source is soil, which contributes >50%. However, AMS measurements on samples collected during the summer from the Zhongguancun region indicate that the contribution of soil to the total carbon concentration is 9.0%. One must combine the two methods of AMS and factor analysis models in the study of atmospheric aerosols (Currie, Klouda and Voorhees 1984).

### Biomedical Science

AMS research on a <sup>14</sup>C-labeled carcinogen for the quantification of carcinogen-DNA adducts was first reported by a group in Lawrence Livermore National Laboratory (Felton *et al.* 1990) with a detection limit of 1 adduct per 1011 normal nucleotides. Collaborating with a group of biomedical chemists in Peking University, we measured DNA adducts with nicotine-derived nitrosamine, 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK). In a recent radioimmunoassay study (Belinsky *et al.* 1990), methylated DNA adducts were detected in rats following treatment with NNK at a low dosage of 1 mg kg<sup>-1</sup> of body weight. However, this dosage is *ca.* 104-fold greater than actual

daily doses of NNK for one snuff dipper or smoker; hence, the human cancer risk posed by NNK is difficult to ascertain accurately. In our experiment, we measured samples of DNA adducts in mice exposed to NNK for a wide range of doses (Li *et al.* 1994a,b), and obtained a linear-logarithmic relation between the number of DNA adducts and dose of NNK. We also achieved an extremely low detection limit of 1 adduct per 10<sup>11</sup> nucleotides for <sup>14</sup>C-labeled DNA adducts. This detection limit is 2–5 orders of magnitude better than other techniques used for quantitative assay of DNA adducts, such as 32P-post-labeling, radioimmunoassay and fluorescence spectrometry. The lowest dosage of 100 ng kg<sup>-1</sup> is approximately equivalent to NNK exposed to a snuff dipper after dipping 1 g of snuff, and a smoker after inhaling 20 cigarettes. The present results show that AMS provides a very sensitive means for measuring DNA adducts using <sup>14</sup>C-tagged xenobiotics.

## CONCLUSION

After the first phase of improvements, PKUAMS shows better performance in <sup>14</sup>C measurements. The fruitful results of its applications in various fields indicate that PKUAMS has become a powerful instrument with which to promote the development of many disciplines in China. Further improvements are being planned and undertaken.

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