THE NEW ^{14}C ANALYSIS LABORATORY IN JENA, GERMANY

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ABSTRACT. The new accelerator mass spectrometry (AMS) Radiocarbon Analysis Laboratory in Jena is described. The laboratory developed a combustion system for solid samples and a CO_2 extraction system for air samples. Thus far, sample preparation, including graphitization, was performed in the laboratory, and the samples were measured subsequently by other AMS facilities. Currently, the laboratory owns a 3MV AMS system from HVEE (Netherlands) that has passed the acceptance tests and will be used for routine ^{14}C determinations in the near future. The AMS system is equipped with 2 ion sources, one suitable for graphite targets and the second for both graphite and CO_2 targets.

INTRODUCTION

Accelerator mass spectrometry (AMS) of radiocarbon is an important and well-established tool in many fields of science (e.g. in archaeology or biomedical applications). One of the major fields of research at the Max-Planck-Institute of Biogeochemistry is the investigation of the local and global carbon cycle of the earth system. With the ability of the AMS technique to determine the carbon isotopic composition of samples of mg size or less, AMS is also applicable to support these investigations. Therefore, the [14]C Analysis Laboratory was formed within the institute in 1998.

Since the year 2000, the [14]C Analysis Laboratory in Jena has been assisting research in the institute by providing state-of-the-art preparation of solid and gaseous samples for ^{14}C measurements. In the first years of the laboratory, the samples were pretreated, combusted, and graphitized at Jena, while the AMS measurements were performed at the Leibniz AMS Laboratory in Kiel, Germany, the Rafter Radiocarbon Laboratory in Lower Hutt, New Zealand, or the Research Laboratory for Archaeology in Oxford, Great Britain.

Below, we describe the sample preparation line, its performance, and the sample management system AMSIS (AMS Information System), which was designed and implemented for controlling the flow of samples through the processing. In September 2003, a 3MV accelerator, manufactured by High Voltage Engineering Europa (HVEE), was being installed and commissioned at the laboratory. The features of this accelerator are summarized and presented together with the first performance measurements.

SAMPLE PREPARATION

Sample Preparation Line

The majority of the samples that were prepared in the laboratory so far were soil and air samples, although other materials like wood were also prepared. The first stage of the sample preparation is chemistry. In the case of soil samples, if required, inorganic carbon was removed. For wood samples, α-cellulose was extracted.

The schematic set-up of the post-chemistry sample preparation line is shown in Figure 1. The heart of it is the UGCS (Universal Gas Collection System) which is used for solid as well as gaseous sam-

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ples. Solid samples enter the sample preparation line through the elemental analyzer, which is a NC2500 (Carlo Erba), consisting of a combustion and a reduction oven, a chemical water trap, and a gas chromatograph (GC) column. We use the conventional set-up, i.e., in contrast to the proposal of the Groningen group, all the CO_2 passes through the GC column (Aerts-Bijma et al. 2001). A small part of the sample mass is used for the IRMS (isotope ratio mass spectrometer), model Delta Plus (ThermoQuest). The major part of the sample is extracted from the helium flow in the cryogenic CO_2 trap of the UGCS and directed into either riglets (reactors) for graphitization, special flasks for the gas source, or alternatively to ampoules for storage. Altogether there are 20 outlet ports, allowing the processing of 20 samples in 1 combustion batch. UGCS has been built in such a way that future connections to other input sources can be easily implemented, e.g., to a laser ablation system.
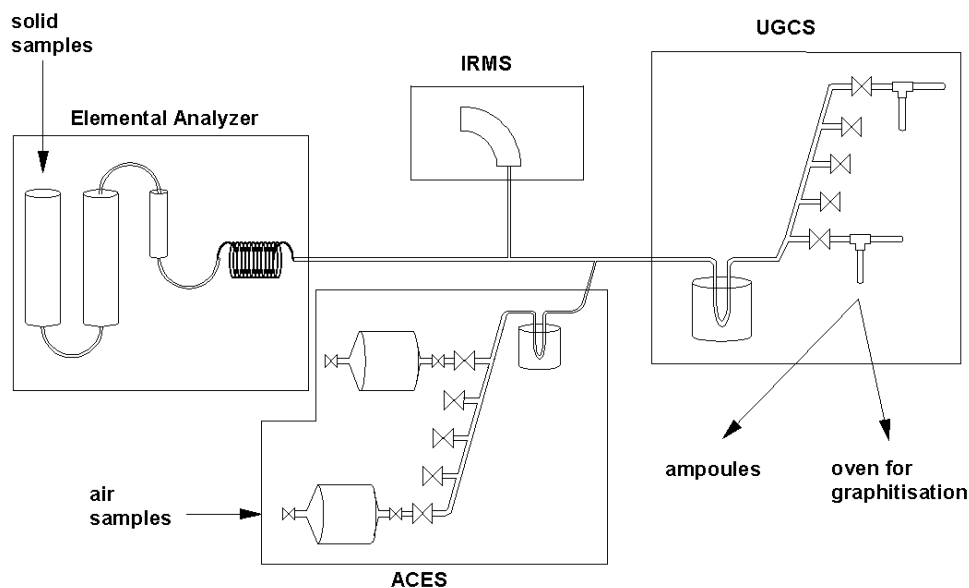

Figure 1 Schematic set-up of the post-chemistry sample preparation line showing the major parts: the elemental analyzer, the IRMS (isotope ratio mass spectrometer), the ACES (<u>A</u>ir-<u>C</u>O₂-<u>E</u>xtraction <u>S</u>ystem), and the UGCS (<u>U</u>niversal <u>G</u>as <u>C</u>ollection <u>S</u>ystem). For more details, see text.

In the air samples, the bottles containing the samples are mounted to the ACES ($\underline{A}$ir-$\underline{C}O_2$-$\underline{E}$xtraction $\underline{S}$ystem), which consists of a manifold for 20 bottles and a cryogenic water trap. The CO_2 is separated from the other gases (nitrogen, oxygen, and argon) in the UGCS cryogenic CO_2 trap and subsequently treated like the CO_2 from solid samples. Each individual extraction takes about 2 hr, limited by the pumping speed of UGCS, which we want to improve in the future.

The standard operation mode is semi-automated, i.e., all valves can be controlled from a switchboard, and only a small dewar with liquid nitrogen has to be positioned manually to the CO_2 trap (for the extraction of CO_2 from helium or air) and the respective sample container (for the transfer of the sample from the CO_2 trap to the sample container). For the extraction of CO_2 from air, an alternative fully-automated mode was developed: all valves in this mode are controlled through a computer interface (National Instruments) and an electronic unit built in-house. The control software is based on Measurement Studio (National Instruments) and is written in the computer language C. Instead of moving a small dewar between first the CO_2 trap and the respective sample container, a large one was designed that permanently cools all sample containers, and only the CO_2 trap is moved pneumatically in and out of the large dewar. The liquid nitrogen of this large dewar is refilled automati-

cally. With this automation, we hope that unattended overnight operation will become a standard routine in our laboratory.

Performance of the Sample Preparation Line

Presently, around 800 samples (not including standards, background, and test samples) have been prepared with the described system, mainly soil and air samples. With the soil samples, we found that it was very important to check whether the combustion oven within the elemental analyzer is really free of carbon from the previous sample. Therefore, after each soil sample we added combustion cycles without any sample and used the IRMS to measure the resulting carbon peak. The combustions without samples were repeated until the peak of the carbon was below 10^{-4} of its usual height. For soil samples with a total mass between 20 and 50 mg, up to 7 empty combustion cycles were required.

Anthracite was used initially for the combustion blank. In the first 15 batches, we reached a mean value of 0.35 pMC (45,500 BP), but starting with batch 16, we used a new piece of anthracite and the mean value increased to 0.55 pMC (41,700 BP) (Figure 2). To avoid the uncertainty due to the sample material, in the last batch (nr 22) we used the IAEA C1 marble standard (Rozanski et al. 1992) and obtained 0.216 ± 0.016 pMC (49,300 BP) as a mean value of the 3 samples. These values are not as good as the ones reached with the sealed ampoule hydrolysis technique (e.g. Nadeau et al. 2001), but are very good compared to published values of other laboratories with a comparable system (e.g. Aerts-Bijma et al. 2001). In the future, it will be checked whether the good values and the low scatter measured with the 3 C1 standard samples of the last batch can be reproduced. As soon as we have more statistics for the background, we will experiment with taking off the combusted CO_2 before the GC column, as proposed by the Groningen group (Aerts-Bijma et al. 2001).
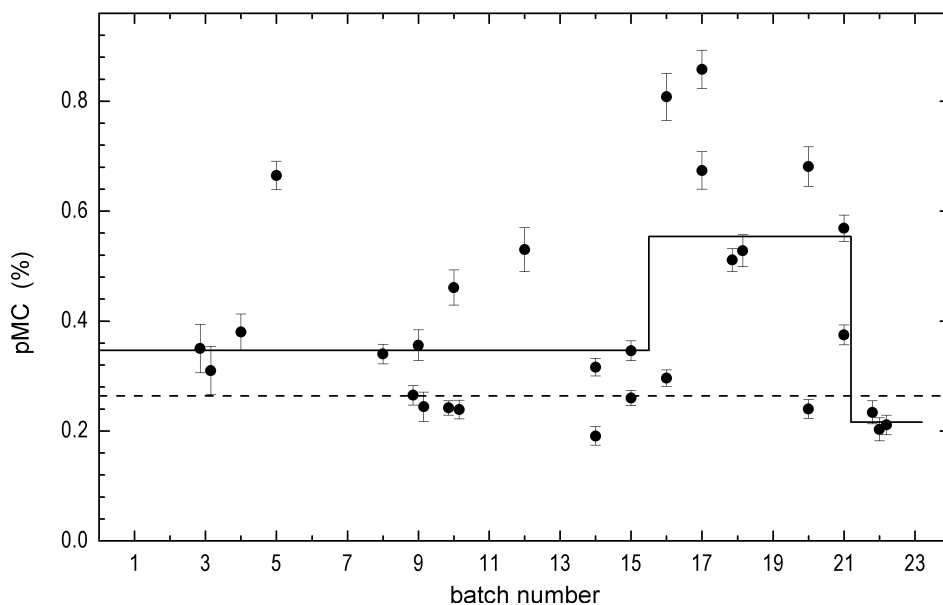

Figure 2 Background levels resulting from samples prepared in Jena, but measured at other facilities. Up to batch 15, the samples originated from a single piece of anthracite, yielding a mean value of 0.35 pMC (45,500 BP). From batch 16 to 21, another piece of anthracite was used and the mean value increased to 0.55 pMC (41,700 BP). In batch 22, the C1 marble standard of the IAEA was used and gave a mean value of 0.216 ± 0.016 pMC. These mean values are indicated by the solid line. The mean value of the graphitization background measured with bottled CO_2 gas (purity 4.8, Linde AG, Germany) is indicated in the figure by the dashed line.

To determine the graphitization background, bottled CO_2 (purity 4.8, Linde AG, Germany) was processed through the UGCS. The mean value graphitization background obtained from 12 measurements was 0.264 ± 0.084 pMC (47,700 BP). The "large" scatter is due to problems with 2 samples. But even without the 2 outliers, the mean value is 0.224 ± 0.040 pMC and, therefore, higher than one of the C1 standard samples, which indicates that our CO_2 either is not be completely free of ^{14}C or there is a problem with contamination. Nevertheless, this mean value is satisfactory for our purpose and our system does not require modifications at the moment.

The reproducibility of processing was checked by using the measured values of the standards. The observed scatter agrees well with the expectations based on counting statistics (Figure 3). As a further test, a set of IAEA standards with different ^{14}C concentrations was used, namely C5 (23.05 pMC) and C2 (41.14 pMC) (Rozanski et al. 1992). Up to now, we processed only 3 samples of each and found a reasonable agreement with the nominal values.
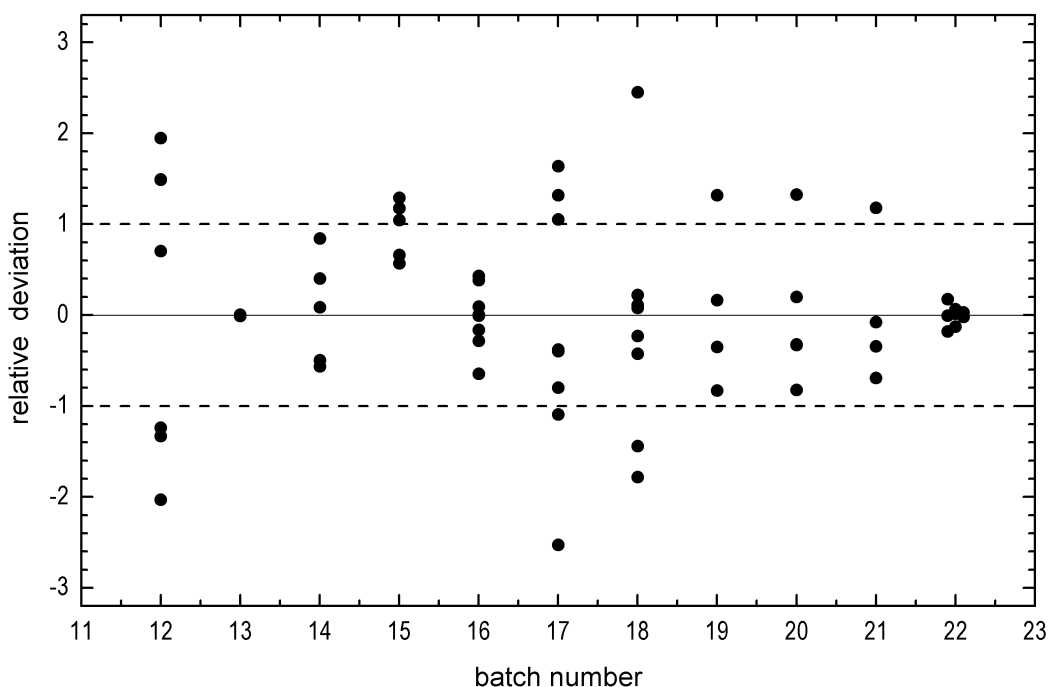

Figure 3 Precision of standards resulting from samples prepared in Jena, but measured at other facilities. Shown are the deviation of the single values from the mean value of the respective batch, divided by their statistical errors. Therefore, ± 1 corresponds to $\pm 1\ \sigma$ and the percentage of 67% found within ± 1 is in good agreement with the expectation for the scatter due to statistical reasons alone.

LABORATORY MANAGEMENT SYSTEM

AMSIS (<u>AMS</u> Information <u>S</u>ystem) is an in-house developed database system designed to allow an efficient management of the workflow in the ^{14}C laboratory (see Figure 4). It was written in MS Visual Basic 6.0 and the data is stored in the institute database IBM DB2.

When samples are submitted to the laboratory, all sample information is stored in the database. Subsequently, AMSIS assists the laboratory staff in preparing lists of samples for the various stages of processing, i.e., chemistry, combustion, CO_2 extraction from gas samples, graphitization, and AMS measurement. It allows listing samples that are in the different stocks awaiting processing. The
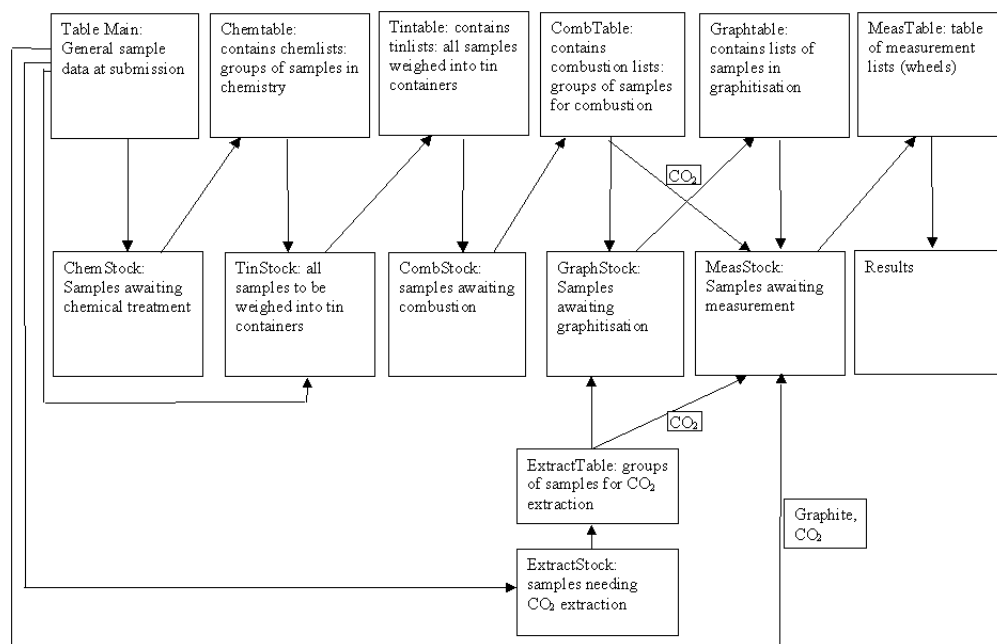
Figure 4 Logical flow chart diagram of AMSIS (<u>AMS</u>-<u>I</u>nformation <u>S</u>ystem). The chart shows schematically the possible paths of the samples from submission to the final results. The upper rows indicates tables where different lists are stored. The lower rows show the different stocks from which samples can be selected for processing.

employment of AMSIS allows optimization of the process by selecting certain samples to be processed in 1 batch and determine their order. This, for example, allows minimizing the possibility of cross-contamination between samples (e.g. when a very old sample would be combusted after a very young one).

Due to the direct transfer of weight from the balances in the AMSIS database and the use of barcodes for labeling the samples, the probability of human errors is largely reduced. The barcodes are printed by AMSIS on barcode printers connected to PCs for the submission, for the test tubes in which samples are chemically processed, and for the Eppendorf vials containing the tin capsules with samples for combustion. After combustion, the CO_2 is stored in riglets that are numbered. If the sample is graphitized, the target wheel positions are stored in the database. AMSIS also allows a fast and transparent comparison according to various criteria and viewing of the "processing tree" of a given sample (the tree representing to what treatment a given sample was subjected).

AMSIS is currently being implemented in the laboratory.

AMS SYSTEM

At our laboratory, a 3MV Tandetron 4130 AMS ^{14}C system was installed by High Voltage Engineering Europa (HVEE), Netherlands, and passed all acceptance tests on 30 September 2003. The system is very similar to those operating in Groningen (Netherlands), Kiel (Germany), and Nagoya (Japan). All these systems operate at a terminal voltage of 2.5 MV and apply the so-called recombinator for simultaneous injection of the 3 carbon isotopes. Detailed information on layout, characteristics, and performance can be found elsewhere (Gottdang et al. 2001).
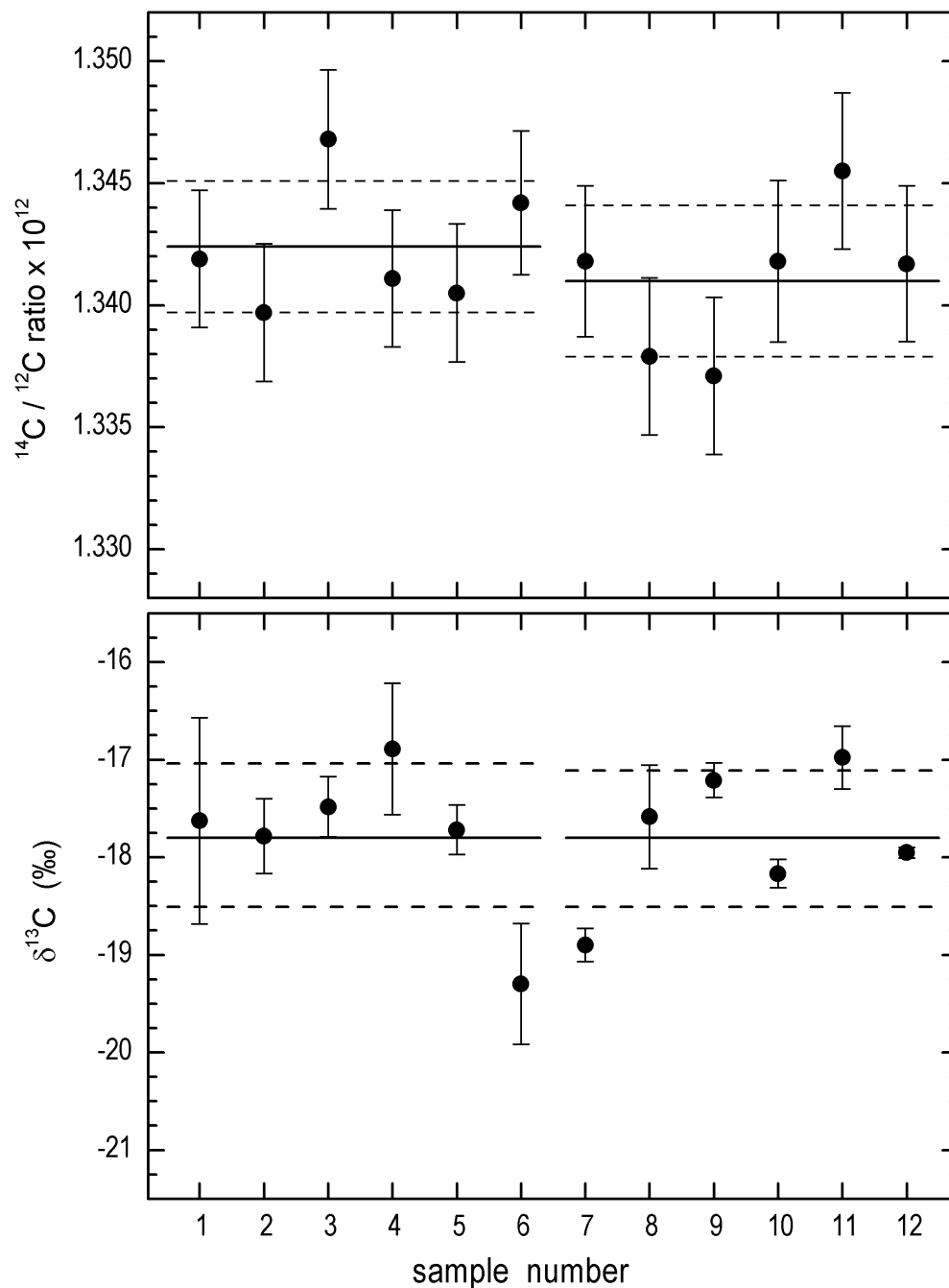
Figure 5 Results of the acceptance test of our system using Ox II targets prepared at the Leibniz AMS laboratory in Kiel, Germany. The upper diagram shows the mean $^{14}C/^{12}C$ ratios measured for each sample and the mean value for each set (i.e. each day). The error bars are calculated from counting statistics and the dashed lines show the 1-σ uncertainty for each set, determined by the scatter of the mean values of the single samples. The lower diagram shows the respective $\delta^{13}C$ values, normalized by setting the mean values of each set to -17.8‰. The error bars are calculated from the scatter of the 4–5 runs of each samples. The solid lines show the mean values and the dashed lines their uncertainty of ±0.73‰ and ±0.70‰.

A major difference with the other AMS systems mentioned previously is the second injector with an ion source model SO-110, in addition to the standard ion source 846 B. The ion source SO-110 is a hybrid negative ion sputter source capable of handling solid graphite as well as gaseous CO_2 samples. For small samples (a considerable number of our samples), the higher efficiency of the gas source is particularly important (Bronk Ramsey et al. 1997). Detailed information on layout, characteristics, and performance can be found in Bronk Ramsey et al. (2004) and references therein. Compared with earlier HVEE AMS systems, the injectors have a higher ion optical acceptance for the isotopic carbon beams. Therefore, we can operate the system with higher ion currents of approximately 50 µA analyzed $^{12}C^-$ under standard conditions.

The ability of the system with the ion source 846 B was demonstrated by measuring the $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios of 2 sets of 6 standard samples (Ox II) precisely and reproducibly. Within 1 set of samples, the runs took place in a cyclical measuring sequence; in each sequence, each sample was measured for 540 s, giving approximately 50,000 ^{14}C counts. For the acceptance tests, 4–5 sequences per set were measured. Set 1 (samples 1 to 6) was measured on 15 September, and set 2 (samples 7 to 12) was measured on 18 September. The mean values of the sets reached a precision of 0.20% and 0.23%, with averaged statistical errors of 0.19% and 0.24%, respectively (see Figure 5). Furthermore, the system proved to have a low background below 54,000 BP. The used material from commercially available graphite rods has given the equal background level at other systems, too (Gottdang 2003).

The precision of the SO-110, operating with CO_2 gas, was tested analogous with 2 sets of 6 samples, measured on 29–30 September each set on 1 day, and reached a precision in $^{14}C/^{12}C$ of 0.48% and 0.44%, with averaged statistical errors of 0.44% and 0.39%, respectively. The lower precision (as compared to the 846 B ion source) is due to the lower currents. The background level was found to be at 43,000 BP.

CONCLUSION

At the ^{14}C Analysis Laboratory in Jena, a sample preparation line has been implemented successfully. This system has demonstrated all requirements needed for our applications. Because the aim of the lab is the support of the in-house scientists, the majority of the samples in the future will be soil and air samples. Our samples are expected to be small in terms of the carbon content, in particular the air samples, although they will have rather high ^{14}C concentrations. Therefore, our future development will concentrate on better precision for small samples.

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