

SAMPLE THROUGHPUT AND DATA QUALITY AT THE LEIBNIZ-LABOR AMS FACILITY

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ABSTRACT. Since our first report on the performance of the Kiel accelerator mass spectrometry (AMS) system and our early work on sample preparation, systems have been built to improve the sample quality and throughput of the laboratory. Minor modifications were also made on the AMS system, mainly in order to reduce the amount of work and time needed to maintain the system in optimal condition. The design and performance of a 20-port reduction system, a pneumatic target press, and a remote alarm unit for the AMS system are discussed, along with an overview of the results obtained during the last year and the procedure used to obtain them. Statistical analysis shows that the contribution of the AMS system to the measuring uncertainty at our current level (0.3% for a modern sample) is negligible.

INTRODUCTION

At the Tucson AMS-7 conference in May 1996 (Nadeau *et al.* 1997), we reported the performance of the accelerator mass spectrometry (AMS) system (accepted from High Voltage Engineering Europa B.V. (HVEE) on September 9, 1995) and the infrastructure needed to support it. After more than a year of operational experience (in June 1997), we report that the accelerator mass spectrometry (AMS) system maintained its excellent stability and that the settings (optimal voltages and currents) still remain constant from experiment to experiment within the ranges mentioned previously. The tandemron-based AMS system, characterized by the simultaneous injection of the three carbon isotopes has been described in several publications (Nadeau *et al.* 1997; von Reden *et al.* 1992, 1994; Gott dang *et al.* 1995; Purser *et al.* 1988; Purser 1992) and will not be reviewed here.

The planned sample throughput of 2000 samples per year (which translates into 2500–3000 targets when standard, blank and duplicate targets are included, excluding test targets) should be feasible without difficulty from the accelerator standpoint. However, feeding the accelerator and keeping it running 24 hours a day, 7 days a week places undesirable strain upon the personnel unless the sample preparation systems have more than sufficient throughput. Consequently, our effort in the past year shifted from the AMS system itself to the logistics of the institute. It is still our desire to improve and better understand the background of the AMS system, presently at 0.05 pMC (Schleicher *et al.* 1998), to study its ion optical properties and improve the stability of certain of its components, but this has a lesser priority at the moment. We report here changes in procedures and equipment made over the last year that result in savings in personnel time and/or increases in sample throughput. An analysis of the measuring uncertainty of the routine samples processed during the past year and their results is also presented.

AMS System Improvements

Routine operation has shown it is necessary to clean the ion source every 6–8 wheels of 57 analyzed targets. It has also become apparent that Penning gauges need to be cleaned 3 or 4 times a year (more often at the ion source). For the gauges located at the entrance and exit of the accelerator, this cleaning procedure means opening the accelerator tubes to air, requiring several hours to pump down the system and to condition the accelerator afterwards. Valves have therefore been installed in order to isolate the gauges from the system during repairs or maintenance. Since the AMS system needs to be at thermal equilibrium to perform at its optimum, and magnets and the accelerator need to be

powered for at least 24 hours before the system can be used for routine measurements; we try to limit the number and length of routine maintenance to these parts and to keep the system at voltage.

Measuring samples 24 hours a day, 7 days a week obviously implies unattended measurements. The system delivered by HVEE was already well protected for such a mode of operation and we believed that the system would safely shut itself down in case of problems. Yet, the desire to make sure that the system was still working (and reduce extra warm-up delays) motivated us to check on it several times a day.

The safety of the AMS system is ensured by a PLC (programmable logic controller), which manages the various digital controls and readouts of the system. Thanks to a modification in its programming by HVEE, this unit now also sends optical signals to an alarm system, built in-house, connected to audio-visual alarms in the laboratory and a stand-alone modem. This unit was designed with as few digital electronic components as possible, protecting it against voltage spikes. It would also have been possible to use a personal computer for this purpose; however, one has to remember the sensitivity of PCs to electric noise such as that created by an accelerator spark. The modem sends a telephone message to a pager, which gives more freedom to the operator on duty.

Sample Preparation Improvements

We have opted for a two-step process where the sample material is first converted into CO₂ (*via* combustion or hydrolysis for organic and carbonate materials), then the CO₂ (stored in transport vessels) is reduced to graphite on a Fe catalyst in a separate system (Vogel *et al.* 1984; Nadeau *et al.* 1997). The graphite/iron powder is pressed into an aluminum target holder soon after the reduction has terminated. Our main objectives in planning the sample preparation were to make the systems flexible, to lower the blank results, and to have an excess capacity so that urgent samples can be dealt with without too much disturbance to the normal schedule. With the concern that any shared section of preparation system can introduce contamination from the memory effect, we have designed modular systems (Vogel *et al.* 1984) where each unit can be isolated or used separately and where the common manifolds are used only for pumping and clean gas handling. A discussion of the contamination associated with each preparation step can be found in Schleicher *et al.* (1998).

CO₂ Production

After proper chemical extraction, organic materials are flame sealed in evacuated quartz tubes (~20 cm long, 3/8" outer diameter) together with pre-baked CuO and silver wool. The sample material is first deposited in a smaller quartz tube to prevent contact with the walls of the outer tube to reduce breaking. The combustion occurs at 900°C in a muffle oven. At present, the quartz tubes are broken inside glass "ball joints" and the CO₂ is transferred to transport vessels. We would like to transfer this operation to the reduction system in the future to avoid the use of transport vessels and the possible related contamination. Carbonate samples are converted into CO₂ in the hydrolysis system described previously (Nadeau *et al.* 1997). However, we are currently investigating different modular systems. Few water samples have been analyzed thus far for the ¹⁴C concentration of their dissolved inorganic carbon (DIC). They were prepared in an automated on-line DIC-CO₂ extraction system connected to a stable isotope mass spectrometer.

Reduction System

With the knowledge gained from the operation of a reduction system prototype (Nadeau *et al.* 1997), a two 10-port stainless reduction system was built. Each port, made of a 3/8" Cajon Ultra Torr steel tee and a 1/4" Swagelock tee welded together connecting a 3/8" quartz tube, a pressure transducer, a

cold finger, a sample port and the manifold, is similar to the prototype in design but not in size. The use of 3/8" quartz reduction tubes and ultratorr tees, instead of 1/4" in the prototype, reduced the reduction time from 5–6 h to 2–3 h. Although this still exceeds the 1.5–2 h reaction time obtained with a 1/2" system, it shows that the influence of gas diffusion as a rate-determining step has been strongly reduced. This also entails less kinetic isotope fractionation and more homogeneous samples. The prototype using rubber-sealed valves (type Nupro Plug valves) showed a memory effect of 0.6% of the previously reduced samples. Using metal-bellows sealed automated valves with Kel-F seats (type Nupro BK) we were able to reduce the memory by a factor of 100 (down to 0.006% of the previous sample). This eliminates the need to flush the system with water vapor between samples. The reduction ovens are temperature controlled individually by a thermocouple feedback loop and their operating temperature can be set individually and collectively, providing more flexibility and faster cycle times. Peltier cooling of the water traps used in the prototype has been abandoned in the new system as the power needed and the heat produced by each element made it impractical for a 20-fold system. The water traps of a line are cooled, at the moment, by a common dry ice cooled Syltherm™ bath raised and lowered by lab-jacks. We are currently developing a water trap system based on a cryo-cooled finger inserted in a copper bar, eliminating the use of cooling liquids. Each port is independently monitored by a pressure transducer (Next Sensors TO5-30-A1), as was the prototype.

Each port described above is self-contained and the sample gas does not have to pass through a common manifold, thus reducing the risks of cross-contamination. Ten reduction units are connected to a 1/2" manifold providing a clean gas supply (O₂, H₂, Ar) and pumping by a three-stage dry pump system, eliminating the need for cold traps. The two manifolds are interconnected only *via* the clean gas supplies through Nupro BK valves.

Pneumatic Target Press

To improve the uniformity of the targets and to ease target preparation, we built a pneumatic press. Targets can be pressed either individually or in the ion source target wheel (59 target positions). To facilitate the use of small amounts of material and reduce the risks of contamination (as observed using different prototypes), the press was designed so that the target holders are filled from the surface to be sputtered (top), which allows the use of short and wide filling funnels. Once filled, the top of the target holder is covered with clean aluminum foil to prevent contamination and the sample material is pressed flush with the surface of the holder by a steel pin pushed from below while a hard surface is brought down from above (*cf.* Fig. 1). This inversion of the pressing process is more complicated than if the target were filled from the back, already pressed to a fixed hard surface, but the advantages seem, so far, to outweigh the problems. A pressure of *ca.* 17 t cm⁻² is adequate for reduced material with an Fe:C ratio by weight of ~2. For commercial graphite, a lower value of 11 t cm⁻² performs best. Tests showed that the ¹²C⁻ current and ¹⁴C/¹²C ratio were not affected by variations in pressure over a wide range (11–30 t cm⁻²). At higher pressures, the material forms a pill, which might detach from the holder when exposed to the Cs beam. The resulting poor thermal conductivity causes an increase in the target temperature during analysis, which decreases the Cs coverage of the target, which in turn decreases the ion yield. The construction of similar presses has been reported before (Aerts-Bijma *et al.* 1997; Cohen *et al.* 1994), however, in both instances the sample powder is loaded from the back of the target holder through a long funnel. The diameter of the hole receiving the C:Fe mixture has been reduced from 2.0 to 1.5 mm, thus reducing the amount of material needed for a certain target thickness by a factor of 2. The behavior of the targets in the ion source was not affected by this change.

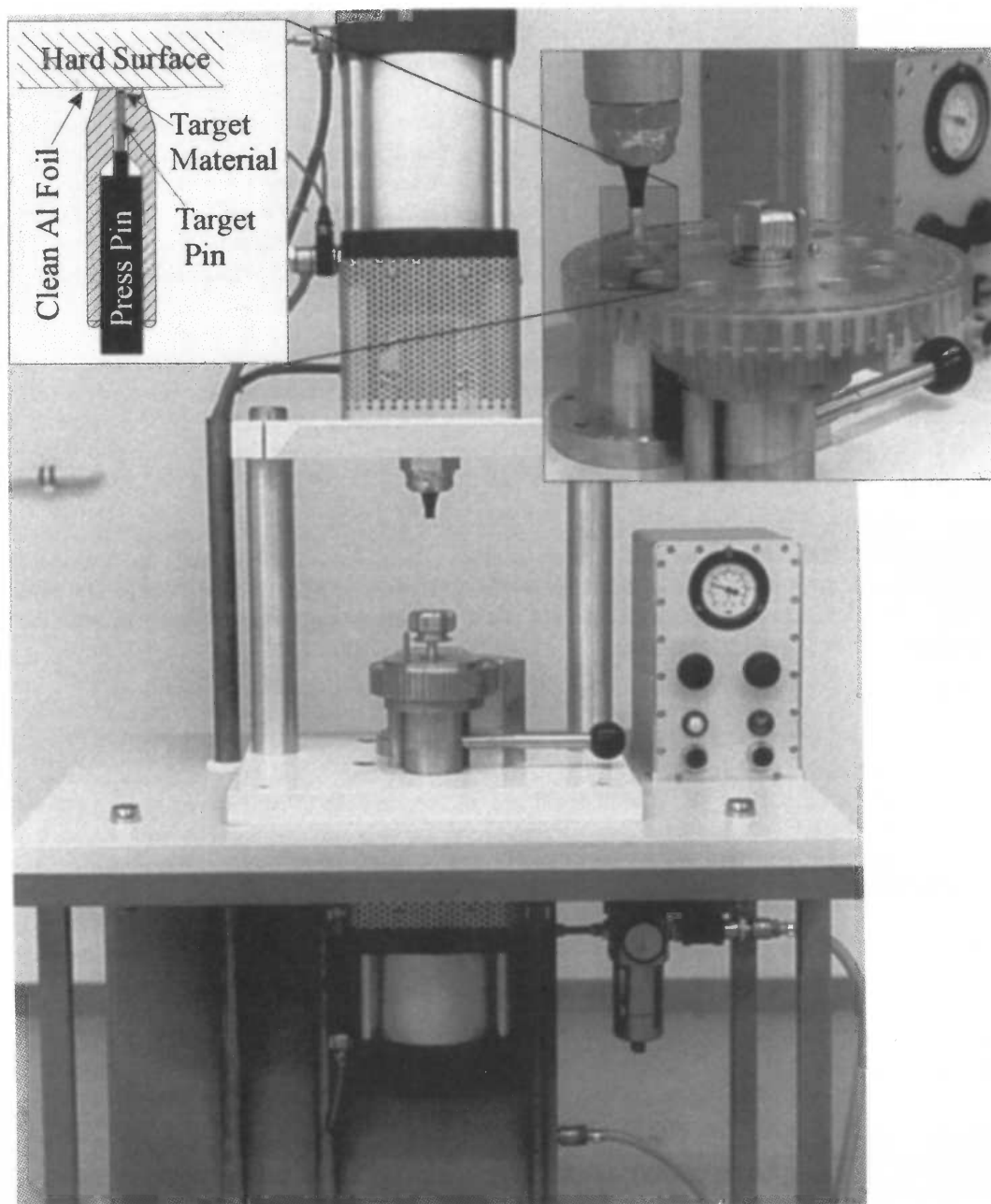


Fig. 1. Pneumatic press for Fe/C targets filled from the top, and pressed flush with the top (A) from below. The inset (B) shows the 59-position target wheel in the press.

METHODS AND RESULTS

We have measured 1934 unknown samples from the acceptance of the AMS system (September 9, 1995) to the end of June 1997 (3700 targets including tests, standards, blanks and duplicates). We measured 1236 of these in 1997, and we are confident that we will be able to reach our goal of 2000 unknown samples per year in our second year of operation.

Measurement Procedure

Since the ion source wheel can accept 58 targets, each routine wheel contains 8 IAEA OX II targets, 6 background targets (3 from carbonate and 3 from organic materials), one chemical graphite blank, one used target as “Cs beam dump” and 42 targets from unknown samples. The complete wheel is measured 8 or 9 times (the first of these passes is considered a surface cleaning procedure and is not included in the final result). During each pass, each target is sputtered on 12 locations for 30 s per position in order to avoid cratering and to maximize the use of target material. Although the AMS system stability and the target homogeneity have proven sufficient to reduce the number of times a target is analyzed (keeping the measurement time constant but reducing the target changing time), we are reluctant to do so since the scatter of the repeated measurement provides us with an additional check on the quality of the result. The complete process takes 70 h per wheel, including target changes between the measurements and pumping time after the wheel has been changed. We normally operate the ion source to obtain an analyzed $^{13}\text{C}^{3+}$ current of 250–300 nA, which provides a <0.3 pMC counting statistic for a modern sample. Targets produced from samples containing 1 mg of carbon can easily withstand three times the sputtering exposure mentioned above. It is tempting to use larger currents and increase the precision of the measurements for the same analysis time. The ion source has shown that stable currents of twice the operational intensity (600 nA $^{13}\text{C}^{3+}$) can be produced without difficulty. More tests are needed to assess the stability of the whole AMS system at higher currents before we can use it for routine analysis.

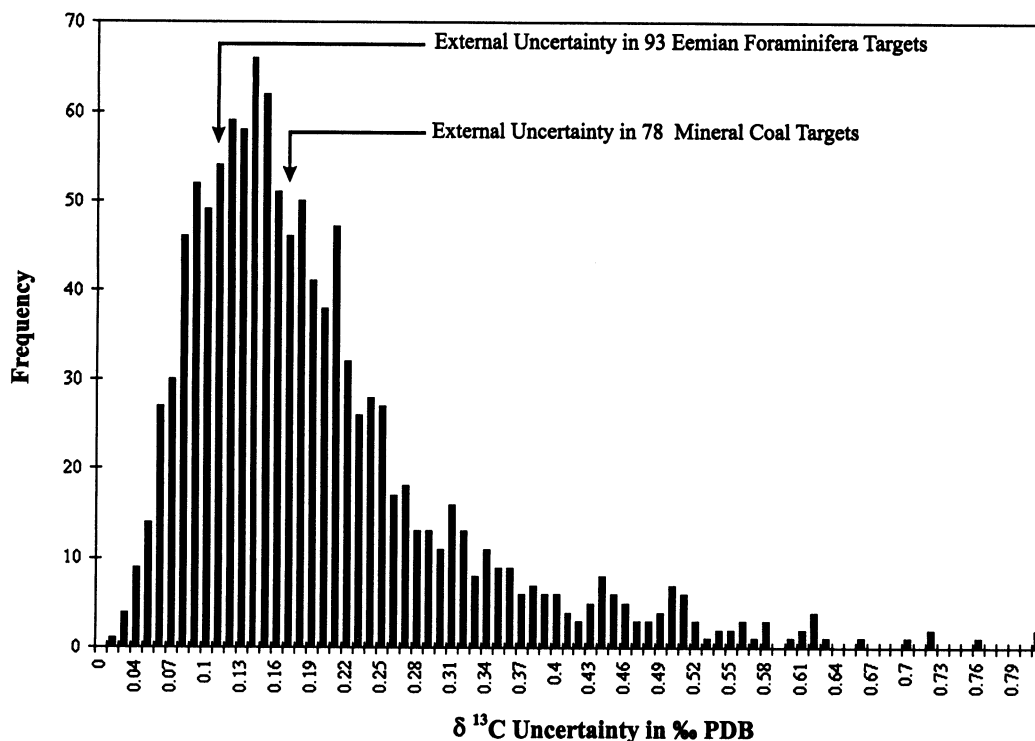


Fig. 2. Distribution of the internal uncertainty of the $\delta^{13}\text{C}$ results from 1164 samples (background and unknown) measured between October 1, 1996 and July 1, 1997. Only measurements related to preparation tests or where problems in target preparation could be identified were removed from the data set. The arrows show the external uncertainty calculated from the distribution of the results of 93 Eemian foraminifera targets and of 78 mineral coal targets.

Results

Due to counting statistics, it is rather difficult to accurately evaluate the reproducibility of the results using $^{14}\text{C}/^{12}\text{C}$ measurements. Although the ^{13}C beam is not analyzed through the same path and is not subject to the last ion optical elements of the spectrometer, the stability of the ratio ($^{13}\text{C}/^{12}\text{C}$) when compared to a standard can indicate the stability of the results. Figure 2 shows the distribution of the $\delta^{13}\text{C}$ uncertainty interval (in ‰ PDB) (calculated from the scatter of the 8 measurements mentioned above) for 1166 unknown and background targets measured from October 1, 1996 to July 1, 1997. The maximum of the distribution, at 0.13‰ PDB (internal uncertainty), corresponds the external uncertainty calculated from the distribution of the results of repeated measurements made on two samples: a sample of mixed foraminifera from the Eem period: $\delta^{13}\text{C} = (1.78 \pm 0.11)\text{‰ PDB}$ (93 repetitions) and a sample of mineral coal: $\delta^{13}\text{C} = (-24.04 \pm 0.17)\text{‰ PDB}$ (78 repetitions).

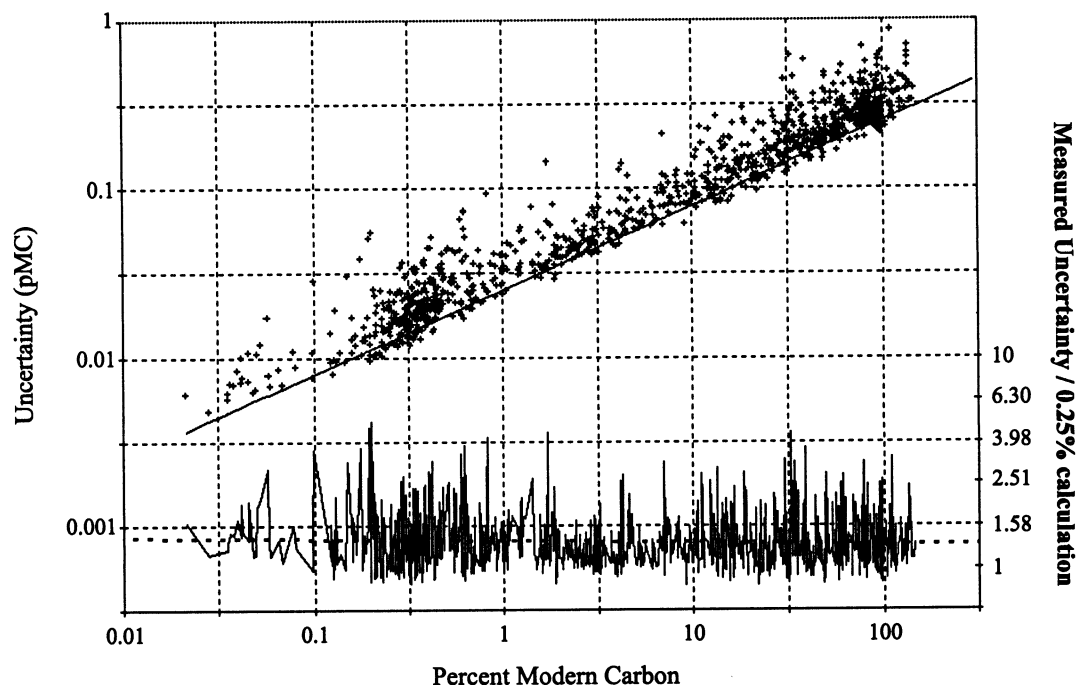


Fig. 3. Log-log plot of the uncertainty in the pMC vs. pMC for 1164 routine measurements made between October 1, 1996 and July 1, 1997. The uncertainty is taken as the maximum of the Poisson counting statistics or the scatter. The solid line corresponds to the Poisson counting statistics of 0.25 pMC for a modern sample when scaled for samples of different ages. The lower curve is the ratio between the uncertainty and the theoretical estimate (logarithmic value). Deviations in the ratio are due to measurements done at lower statistics (shorter measuring time or lower current) or to a larger scatter (non-Poisson) in the 7–8 values used to calculate the final results.

Although this might be overly conservative (Currie 1994), we take as standard deviation for ^{14}C measurement the larger of the Poisson counting statistics or the scatter of the 8 individual measurements (Donahue 1987). Figure 3 shows the error on the measured pMC *versus* the pMC result itself for 1164 routine measurements. The theoretical curve assumes that each sample was measured to a counting statistics of 0.0025 pMC (160,000 counts) for a modern (100 pMC) sample. The fact that some points lie below that curve means that, in several cases, we analyzed the targets for longer than what would have been needed to obtain 160,000 counts. The ratio of the uncertainty in the measurement to the the-

oretical estimate (difference of the logarithm) would increase for results from younger materials if there were a systematic scatter due to instabilities in the AMS system or inhomogeneities in the target materials. The fact that this ratio, if anything, decreases for younger samples probably indicates that the non-Poisson component of the error is smaller than the detection limit of this test, which is in agreement with the 0.13‰ obtained from the ^{13}C uncertainty distribution for the system contribution to the measuring uncertainty.

CONCLUSION

The laboratory is operating, in 1998, at the planned throughput of 2000 unknown samples per year. Yet, more work is required to reduce the amount of work needed to produce the targets and measure them. The new reduction system and target press described above already facilitate target production and the automation of the reduction system (planned for the end of 1997) should furthermore decrease the workload. Analysis of the statistics of routine sample measurements during the past year distinctly shows that it is possible to routinely measure down to 0.25–0.3 pMC precision for modern samples with our equipment. It also shows that the patience of the operator (counting statistics translating into accelerator time) is, at the moment, an important limitation to the improvement of the measurement precision.

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