ENVIRONMICADAS: A MINI ^{14}C AMS WITH ENHANCED GAS ION SOURCE INTERFACE IN THE HERTELENDI LABORATORY OF ENVIRONMENTAL STUDIES (HEKAL), HUNGARY

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ABSTRACT. A more developed and modern technology replaced the old radiocarbon measuring methods in Hungary, based on isotope separation by accelerator mass spectrometry (AMS) and not on activity measurements. In summer 2011, the EnvironMICADAS was successfully installed in the Laboratory of HEKAL, Debrecen, Hungary. In this project, a multipurpose gas-handling system was developed for the gas ion source of EnvironMICADAS at ETH Zürich, designed for the measurement of small environmental origin samples (<50 μg carbon) with moderate precision requirements. The ultimate aim is an automated device for high sample throughput. Since its final installation and first year of operation, over 2000 graphite targets were analyzed. Long-term stability of the instrument is confirmed through measurements of the Ox-II standard and processed blank targets during the first half of 2012.

INTRODUCTION

Radiocarbon dating is widely applied in environmental protection, archaeology, geology, hydrology, climatology, and many other essential scientific topics all over the world. In Hungary, since the 1980s ^{14}C measurements have been applied in archaeology as well as nuclear environmental monitoring (Csongor and Hertelendi 1986). The ^{14}C laboratory of ATOMKI has used the gas proportional counting (GPC) method for high-precision ^{14}C dating for more than 3 decades and has the necessary equipment and experience to handle all kinds of archaeological and environmental samples. This knowledge and tradition provided a very solid base for the establishment of a new AMS ^{14}C facility in the Hertelendi Laboratory of Environmental Studies (HEKAL), Debrecen, Hungary.

In 2011, the first accelerator mass spectrometer (AMS) was installed in Hungary, supplanting but not replacing the more traditional counting methods, based on activity measurements. The advantage of AMS is that it requires much smaller sample quantity (0.01–100 mg) than GPC (1–100 g), which significantly limited the scale of possible applications and research fields (e.g. Burr and Jull 2009). In addition, the AMS technique can give at least 10 times higher throughput (number of samples/week) compared to the radiometric method.

ETH Zürich (ETHZ) and HEKAL have identified the need for a further-improved AMS machine dedicated to ^{14}C studies in connection with environmental research, in particular one equipped with a gas inlet system to handle CO_2 sample material. The 2 teams agreed to undertake a collaboration to develop such an optimized AMS machine for environmental ^{14}C dating studies, referred to as EnvironMICADAS on the basis of the MICADAS AMS concept (Synal et al. 2007; Wacker et al. 2010).

DEVELOPMENT OF ENVIRONMICADAS

The EnvironMICADAS system was successfully developed at ETHZ between the spring of 2010 and spring of 2011. This AMS is very similar to the DatingMICADAS that was recently installed in Mannheim, Germany (Kromer et al. 2013), but the gas ion source applications would be more preferred on the EnvironMICADAS. In April 2011, factory acceptance tests were successfully com-

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pleted at ETH Laboratory in Zürich. A total of 110 samples were measured, including 21 NIST oxalic acid I, 35 NIST SRM 4990C oxalic acid II reference material standards, 6 IAEA-C7, 6 IAEA C-8, and 39 processed blank samples (fossil borehole CO_2 gas from Linde, Répcelak, Hungary). Three samples were not measured because of low currents. These 3 failed targets showed that newly developed graphitization lines in ATOMKI had some fluctuations in the beginning. A summary of the 104 target measurements are listed in Table 1.

Table 1 Acceptance test summary of EnvironMICADAS.

Investigated parameters	Result ($\pm 1\sigma$)
Extracted ion current ($^{12}C^{-}$)	44.2 ± 7.8 μA
Ion transmission through the stripper ($^{12}C/^{12}C_L$)	37.9 ± 0.9%
Oxa-II normalization standard (NIST SRM 4990C)	–2355 ± 17.9 yr BP
Oxa-I NIST standard (–313 yr)	–314.5 ± 26.2 yr BP
IAEA-C7 reference material (49.53 pMC)	49.43 ± 0.11 pMC
IAEA-C8 reference material (15.03 pMC)	15.17 ± 0.05 pMC
Blank samples	46,300 ± 1300 yr BP
Highest blank target	42,500 yr BP
Lowest blank target	50,000 yr BP

The new AMS system fulfils all the requirements needed for high-precision ^{14}C measurement as listed below:

- Throughput: 2 samples per operation hour averaged over 24 hr (minimum 40 per day).
- Minimum precision: 0.25% at 1 Modern, 0.75% at 0.1 Modern.
- Minimum accuracy: 0.3% for 1 Modern, 0.8% at 0.1 Modern.
- Minimum negative ion beam current: 40 μA, $^{12}C^{-}$ from the ion source.

The basic parameters of the AMS instrument are shown in Figure 1.

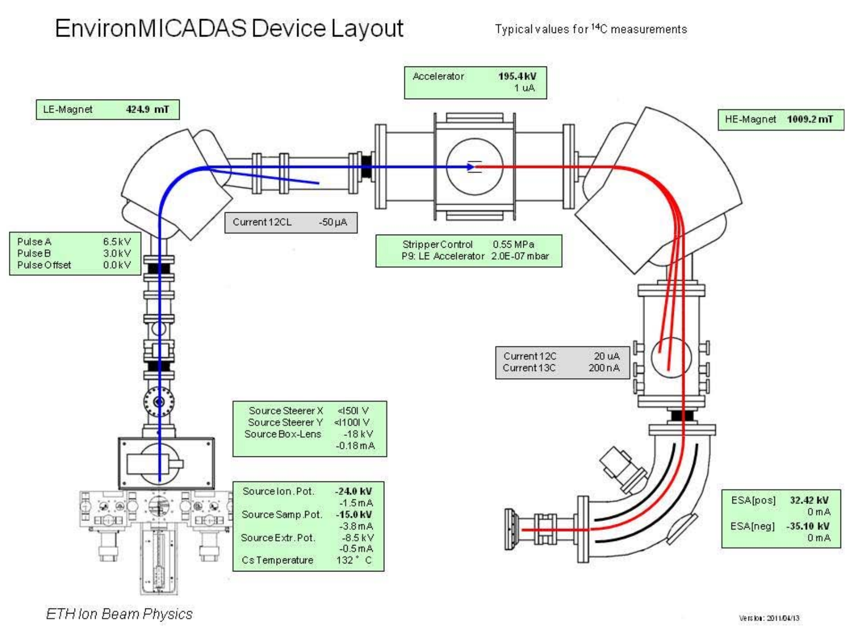

Figure 1 EnvironMICADAS device layout and typical values for ^{14}C measurement

In the summer of 2011, the EnvironMICADAS was successfully installed at the Laboratory of HEKAL, Debrecen, Hungary. The AMS is installed in half of a 144-m^2 ground-floor laboratory hall, including all the necessary supporting infrastructure, equipment, and the gas ion source interface. The new AMS hall has a wide-door direct access to the outside, which significantly facilitated the installation. The room is air conditioned and filtered; the cooling water flows through a closed-loop cooling system and returns to the MICADAS to save deionized water. A photo of the final installation is given in Figure 2.

Figure 2 EnvironMICADAS installed in HEKAL, Debrecen, Hungary

Some initial problems arose with the sophisticated sample-changer system of MICADAS at the beginning of the operation, but after some fine-tuning and replacement of a few small components, the machine is running without problems. The most sensitive part of the ion source seems to be the connector of the Cs reservoir and the Cs feeding line (nozzle), but with careful handling this is also reliable. The ion source is now running reliably and maintenance is usually required every second month of non-stop operation. It takes only about 1 day for a source cleaning and reloading of Cs, before measurements of real samples can be performed again. The most serious problem during the installation of the Debrecen MICADAS was the failure of the Heinzinger type 200kV power supply of the accelerator. Since it was repaired in the Heinzinger factory, this unit works without problems.

Development of a Gas Handling Line for EnvironMICADAS Gas Ion Source

There is great potential for direct CO_2 gas AMS measurements, e.g. for environmental applications, which often make it necessary to perform many ^{14}C analyses of small carbon fractions (aerosols, stalagmite layers, soil organic components). For these applications, often typically <50 μg carbon is available per sample, and graphitization yields are frequently reduced by interfering reaction gases, unless the gas is extremely clean. In this project, a multipurpose gas handling system was developed for the gas ion source of Environ-MICADAS at ETH Zürich that is designed for the measurement of small environmental origin samples (<50 μg carbon) with moderate precision (~1.0% relative error on a modern sample) requirements aiming an automated device for high sample throughput (Figure 3).

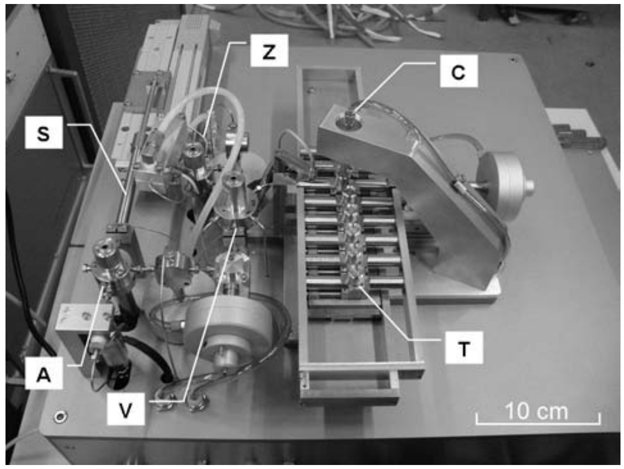

Figure 3 Top view of gas ion source interface system (ETHZ): A: switching valve to inject gas into the AMS; S: gas injection syringe; V: multiport selection valve; Z: zeolite trap valve; T: sealed tube magazine; C: tube-cracker system.

The core of the versatile gas handling system is a stepper-motor-driven syringe that pushes the sample CO_2 mixed with helium continuously into the gas ion source. As the ideal dilution rate is 4% CO_2 in He, the interface gives the possibility to split and vent the unnecessary part of the CO_2 sample if it would be suddenly too much (>100 μg) for the maximum capacity of the syringe. While previously only an ampoule cracker served as a sample supply for the gas interface, samples can now be provided in 3 additional ways with the present setup (Figure 4). Selection between the different CO_2 sources is simply achieved through a multiport valve. For blank, standard, and test measurements, 2 gas bottles with 4% CO_2 in helium have been installed. One bottle contains ^{14}C-free CO_2 and the other one combusted OX-II standard. This OX-II gas mixture is made in ATOMKI from NIST 4990C oxalic acid standard material, as it was combusted in gram amounts in our conventional ^{14}C sample preparation line. The stable isotope $\delta^{13}C$ value (vs. PDB) was measured of the produced Ox-II CO_2 gas using a ThermoFinningan™ Delta XP Plus mass spectrometer, and 0.4 L of the gas was transferred and diluted by He carrier gas into an all metal gas bottle (1 L volume gas can, Messer Co. Ltd.). At the end of the dilution process, the final total pressure is 10 bar in the gas can bottle. The gas ion source interface syringe can be filled with the prepared gas mixtures for well-repeated tests as well as standard and blank measurements. Secondly, samples are combusted in an elemental analyzer (EA) and the gas is transferred to the syringe via a zeolite trap. Thirdly, CO_2 is released from carbonates or water samples with phosphoric acid in septum-sealed vials from where it is transported into a He flow to the same trap as is used with the EA. A large effort has been placed on the automation of the sample introduction systems to allow efficient ^{14}C measurements. Unattended ^{14}C measurements of gas samples are now possible (Wacker et al. 2013).

DATA HANDLING AND DATA REDUCTION, REPORTING THE RESULTS

The data storage framework that follows the MICADAS ^{14}C measurement from the onset of the unknown sample to the final result is a great advantage of the system. All required data and information are stored in a MySQL relational database management system. The data storage and handling performs with the help of an application ecosystem, which was developed by the members of Ion Beam Physics, ETH-Zürich.

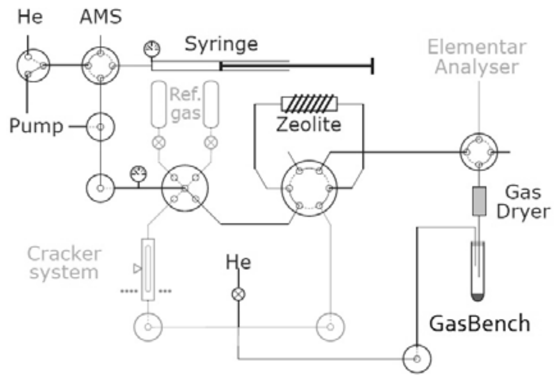

Figure 4 Layout of the sample inlet connection options of the versatile gas interface of the EnvironMICADAS (round symbols show switches and/or multiport valves).

Table 2 Summary of the typical main parameters of the gas ion source interface.

Basic parameters of the system	Typical value/description
Sample injection	Pure CO_2 (4%) in He flow
Sample size	0.005–0.1 mg C
Sample transfer	Sealed tube, EA, GasBench
Ion current in MICADAS	15 µA C^{-1}
Controlling program	Enhanced LabVIEW-based driver software
Throughput	5–20 min/sample (sample-size dependent)

LaMa laboratory management software is able to store and handle all the sample-related information: customers, projects, samples, preparations, and pressed targets. LaMa helps us to trace the evolution of the samples until pressed targets are set into a measurement magazine. In case of a typical measurement on the EnvironMICADAS, the sample magazine contains 22 samples, including at least 2 known-age standards and 2 processed blanks. The definition of the list of samples in the magazines is produced using the *PrepMag* magazine preparation software. Using this tool, one can fix the position of the targets in a magazine, i.e. the measurement sequence. Target positions and magazine information is written back to the sample/target information in the database.

The measurement process of the EnvironMICADAS is controlled by software called *Squirrel*. This software loads the sample list for the magazine from the MySQL database system and sets up the measurement automatically, according to the predefined parameters. Maintenance and/or service of the sample changer and vacuum system are also assisted using the Squirrel software. All targets of a magazine are measured at least 4 times (called “passes”) depending on the required precision. One pass means that all of the targets in the magazine are put into the ion source and measured once, one by one in a predefined order (see PrepMag). A single measurement (called “run”) of 1 target is divided into 10 cycles of 30–60 s long each (depending on the required precision and the state of the system). The different kinds of collected data during 1 cycle are handled as an individual unit during the evaluation process.

The visualization and monitoring of the measured/stored data during the measurement and tuning/scanning processes is possible using the *Nemo* software. Finally, the *Bats* software is used for data evaluation and analysis (detailed information in Wacker et al. 2010). Bats provides the MICADAS measurement results after all the necessary corrections and calculations in conventional ^{14}C age and fraction modern (Fm) units.

RESULTS

Since its final installation, in the first year of operation more than 2000 graphite targets have been analyzed using the new AMS system in Debrecen. Long-term stability of the instrument can be demonstrated via the variability of the Oxa-II normalization standard and the processed blank targets during the first half of 2012 (Figure 5). All the measured targets were prepared using a refined sealed-tube graphitization method (Rinyu et al. 2013).

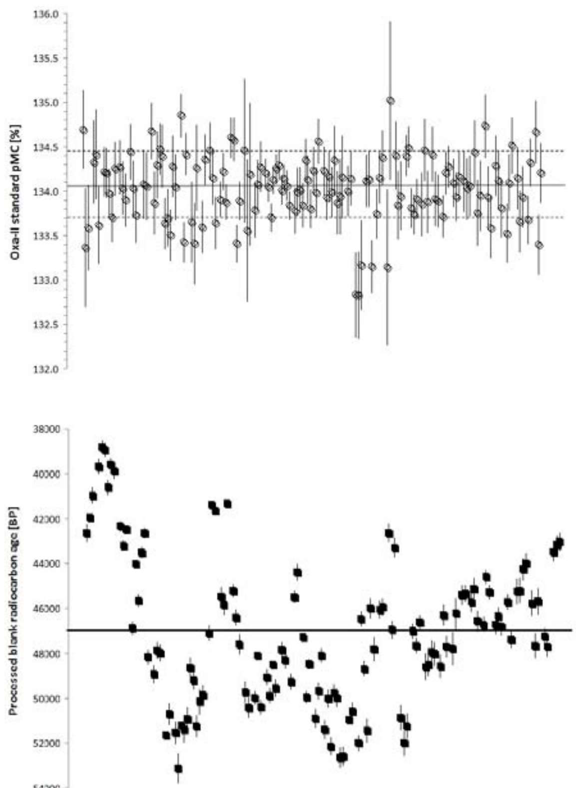

Figure 5 Half-year stability of Oxa-II (upper) and processed blank; (lower) signal from EnvironMICADAS in order of measurement date.

Normally, 3 standards (oxalic acid II NIST 4990C) are measured in a single magazine (22 targets), for normalization and monitoring the stability of the system. The mean value of the standards corrected by the AMS-measured $\delta^{13}C$ is applied for normalization of $^{14}C/^{12}C$ ratios. In the course of the test period, during our early measurements, we put more standard targets per magazine. Figure 5a shows the pMC values for 137 standard targets measured in 37 magazines in the first half of 2012. The calculated standard deviation of the mean is ±0.376 pMC (2.8‰), which shows good agreement with the average value of measurement errors calculated according the counting statistic by Bats (0.332 pMC, 2.5‰).

Processed blank targets were prepared from fossil CO_2 gas ($\delta^{13}C$ = –3.78‰, purity 4.5) from Répcelak (Linde). Figure 5b shows the ^{14}C ages of 122 blank targets measured in 37 magazines in the first half of 2012. During this period, the parameters of the ion source and the overall MICADAS were tuned progressively. A cyclicity of better and worse blank results is visible in the presented half-year period according the source revisions. The freshly cleaned source after a source revision always gave a bit better (lower) blank than later when it was more used and dirty. Every magazine has its own blank targets (at least 3 of the 22 targets in a magazine), so the blank correction is always valid for the actual measurements. The time evolution of the scatter in the measured data reflects this continuous tuning process well. The average processed blank value is ~47,000 yr.

SUMMARY

In 2011, a new AMS system based on the Zürich MICADAS technology was installed in Debrecen. The system was successfully developed at ETHZ between spring 2010 and spring 2011. Finally, in April 2011, the factory acceptance tests were successfully executed at ETH Laboratory in Zürich. In summer 2011, the EnvironMICADAS was successfully installed in the Laboratory of HEKAL. Our machine performs well and demonstrates good precision on recognized standards and low backgrounds.

For this project, a multipurpose gas handling system was also developed for the gas ion source of EnvironMICADAS at ETH Zürich that is designed for the measurement of small environmental origin samples (<50 μg carbon) with moderate precision requirements aiming for an automated device with high sample throughput. While previously only an ampoule cracker served as a sample supply for the gas interface, samples can now be provided in 3 additional ways (elemental analyzer, reference gas bottles, and gas bench).

Since its final installation, in the first year of operation more than 2000 graphite targets were analyzed using the new AMS system in Debrecen. The long-term stability of the instrument is excellent. To distinguish the new AMS ^{14}C data from the old, but still reliably running radiometric gas proportional counting (GPC) ^{14}C results from Debrecen, the Debrecen AMS lab code has the "DeA-" prefix while "Deb-" is reserved for the old GPC method (Csongor and Hertelendi 1986).

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