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^{14}C ANALYSIS AND SAMPLE PREPARATION AT THE NEW BERN LABORATORY FOR THE ANALYSIS OF RADIOCARBON WITH AMS (LARA)

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ABSTRACT. The University of Bern has set up the new Laboratory for the Analysis of Radiocarbon with AMS (LARA) equipped with an accelerator mass spectrometer (AMS) MICADAS (MIni CArbon Dating System) to continue its long history of ^{14}C analysis based on conventional counting. The new laboratory is designated to provide routine ^{14}C dating for archaeology, climate research, and other disciplines at the University of Bern and to develop new analytical systems coupled to the gas ion source for ^{14}C analysis of specific compounds or compound classes with specific physical properties. Measurements of reference standards and wood samples dated by dendrochronology demonstrate the quality of the ^{14}C analyses performed at the new laboratory.

INTRODUCTION

Analysis of radiocarbon (^{14}C, half-life 5730 yr) has wide applications in archaeological dating, environmental research, life science, and other fields. The University of Bern has a long history of experience in precise ^{14}C measurements based on the conventional gas proportional counting laboratory founded by Hans Oeschger more than 50 yr ago (Houtermans and Oeschger 1958). Due to the demanding procedure involved in preparing the counting gas from the organic samples and to the long counting time to obtain reliable statistics, the throughput and required carbon mass were both limiting factors of this technique. During the last 2 decades, enormous technical development in accelerator mass spectrometry (AMS) has been achieved with the breakthrough of the small device MICADAS (MIni CArbon DAting System) (Synal et al. 2007; Synal and Wacker 2010; Synal 2013). This instrument is comparable in terms of precision and detection limit with both conventional decay counters and large AMS systems. Moreover, it offers further advantages due to its simplicity and low requirements of sample amounts and process time. In order to strengthen the application of ^{14}C as dating tool for the Oeschger Centre for Climate Change Research, the University of Bern consequently decided to set up a MICADAS system to provide the long-term infrastructure for in-house ^{14}C analysis. The focus of the new laboratory is twofold. Firstly, the access to routine ^{14}C analysis for archaeology, climate research, and other disciplines will be improved on site. Secondly, new hyphenated (i.e. coupled) analytical systems shall be developed for on-line separation and ^{14}C detection of specific fractions or individual compounds (Wacker et al. 2013a). This article describes the instrumentation of the new Bern Laboratory for the Analysis of Radiocarbon with AMS (LARA), which became operational in May 2013, and first quality assurance measures.

INSTRUMENTATION

The small AMS system MICADAS allows ^{14}C analyses with comparable accuracy and precision compared to larger AMS facilities. The simplified instrumental setup reduces running costs and service efforts (Synal et al. 2007; Synal and Wacker 2010; Synal 2013). The ion source was recently improved for both graphite and gas targets (Fahrni et al. 2013). The magazine holds up to 40 samples. Under stable measurement conditions, ~60 and ~15 μA $^{12}C^-$ currents are typically achieved

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for targets of solid graphite and gaseous carbon dioxide, respectively, but even higher currents are possible. The acceleration and charge reversal is performed with terminal voltage of 200 kV and nitrogen stripping, resulting in a transmission of 40%. Data reduction is performed with the program BATS (Wacker et al. 2010a). Figure 1 shows the MICADAS at the University of Bern.

Our research group has a strong background in the measurement of small ^{14}C samples with a gas ion source at the MICADAS (Ruff et al. 2007) in collaboration with ETH Zurich. Separation and sample combustion instruments were directly coupled with the gas source (Perron et al. 2010; Ruff et al. 2010) with applications to carbonaceous aerosols in the atmosphere and in glacier ice (Sigl et al. 2009; Szidat 2009a,b; Zhang et al. 2012). A particular focus was on building and refining of an automated gas interface (Wacker et al. 2013a), which enables the transfer of carbon dioxide to the gas ion source from different sources, such as sealed glass ampoules, an acidification device for carbonate samples (Wacker et al. 2013b), as well as an elemental analyzer (Ruff et al. 2010) or other combustion instruments (Perron et al. 2010).

For routine dating, a new sample preparation laboratory was installed and equipped with instruments dedicated for ^{14}C analysis at the University of Bern. For production of solid targets with a typical carbon mass of 1 mg, an automated graphitization equipment (AGE) was installed (Němec et al. 2010a,b). This device combines an elemental analyzer with seven reduction reactors fully controlled by a LabVIEW program (National Instruments Inc). For sample pretreatment of most material such as plant remains, macrofossils, bulk sediment, and charcoals, an acid-base-acid (ABA) procedure is performed at 60°C using 0.5 mol/L HCl, 0.1 mol/L NaOH, and 0.5 mol/L HCl for 8 hr each or less, depending on sample stability. After washing with ultrapure water (18.2 MΩ·cm at 25°C, TOC <3 ppb) to pH>4, the samples are dried at 60°C overnight. Cellulose is extracted from wood samples using the BABAB method, i.e. a modified ABA procedure at 75°C for all steps (Němec et al. 2010b): the sample is treated in 4% NaOH overnight, followed by three repeated sequential treatments in 4% HCl and 4% NaOH of 1 hr each; then several bleaching steps of 30 min each using 5% $NaClO_2$ and 2 drops of 4% HCl are performed until the color of the wood samples turns white.

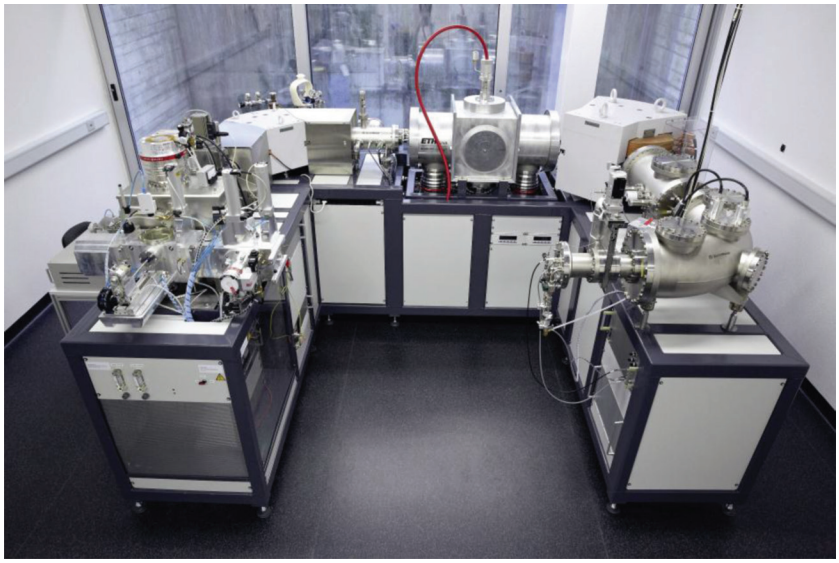

Figure 1 The MICADAS at the new Bern Laboratory for the Analysis of Radiocarbon with AMS (LARA). Photo: A Boutellier.

RESULTS AND DISCUSSION

The performance of the MICADAS was assessed using IAEA standards C4–C7 (Le Clercq et al. 1998) after combustion and graphitization by the AGE as unknowns. In order to guarantee traceability of the results, ^{14}C-free materials and the primary NIST standard oxalic acid II (SRM 4990C) were used for blank subtraction, standard normalization, and correction for isotope fractionations after application of the same preparation as described before (Wacker et al. 2010a). Tables 1a and 1b show the ^{14}C and ^{13}C results of repeated determinations over 4 months. For all of these standard materials and both isotopes, the measured values are not significantly different from the reference values (all within 95% confidence level). Even if not statistically significant, the measured ^{14}C of C6 seems to tend towards lower values than the reference, which will be observed in detail in the future. The ^{14}C analysis of C4 indicates the detection limits of the system applying combustion and graphitization. It was improved by changing the blank material from brown coal or anthracite to sodium acetate (Sigma-Aldrich, No. 71180) and monobasic potassium phthalate (Fluka, No. 96148), as the latter chemicals neither absorb volatile organic compounds nor carbon dioxide from the laboratory air so that very low blanks could be produced with high reliability ($F^{14}C$ 0.0018 ± 0.0005, not blank-corrected, n = 7). Under these conditions, dating is possible up to 52 kyr BP. The $F^{14}C$ measurement uncertainty of non-background materials includes contributions from counting statistics of the sample, uncertainties from blank subtraction, standard normalization and correction for isotope fractionations, as well as an additional uncertainty contribution of 1.5‰. The last uncertainty term accounts for the day-to-day variability of the ^{14}C in general or changing blanks of the capsules used in the elemental analyzer during graphitization. It is estimated from the scatter of individual standard means based on chi-squared tests that compares the uncertainty of all other uncertainty terms with the observed standard deviation of the mean (Wacker et al. 2010a). The standard deviation of all ^{14}C analyses for C5, C6, C7, and oxalic acid II over several measurement runs is comparable to the average measurement uncertainty. This confirms that all uncertainty components are considered appropriately including the additional uncertainty contribution. The standard deviation of the $\delta^{13}C$ reveals that this isotope can be determined with the MICADAS within ~1.2‰ on average for samples of equal size (i.e. based on solid targets with a typical carbon mass of 1 mg).

In order to evaluate the quality of wood dating, a series of 10-yr segments of mid-European oak samples dated between 470 and 9660 yr BP with dendrochronology were prepared to cellulose as previously described and measured for ^{14}C. The additional blank during chemical preparation was

Table 1a Radiocarbon analysis of IAEA standards (Le Clercq et al. 1998) with NIST standard oxalic acid II from n determinations of 5 measurement runs between March and August 2013 with average measurement uncertainty and standard deviation of all analyses (both calculated referring to the single analysis).

Standard	^{14}C reference [$F^{14}C$]	^{14}C measured [$F^{14}C$]	Av. uncertainty [$F^{14}C$]	St. deviation [$F^{14}C$]	n
C4 (wood)	(0.0020–0.0044)	0.0017*	0.0003*	0.0002*	4*
C5 (wood)	0.2305 ± 0.0002	0.2304	0.0010	0.0014	8
C6 (sucrose)	1.5060 ± 0.0011	1.4994	0.0040	0.0065	9
C7 (oxalic acid)	0.4935 ± 0.0012	0.4950	0.0015	0.0018	10
Oxalic acid II	1.3407 ± 0.0005	1.3407#	0.0039	0.0026#	22

*Only measurements after change of the blank material (see text) were considered because of the improved detection limit.
#For traceability, $F^{14}C$ is normalized to the reference value (Wacker et al. 2010a); the uncertainty of this normalization (on average 1.5‰) was added to the standard deviation for comparison with the other standards.

Table 1b $\delta^{13}C$ analysis of IAEA standards with NIST standard oxalic acid II from *n* determinations of 5 measurement runs between March and August 2013 with standard deviation of all analyses (calculated referring to the single analysis).

Standard	^{13}C reference [‰]	^{13}C measured [‰]	St. deviation [‰]	*n*
C4	−24.0 ± 0.1	−23.3	1.7	11
C5	−25.5 ± 0.7	−24.7	1.0	8
C6	−10.8 ± 0.5	−10.0	1.4	9
C7	−14.5 ± 0.2	−13.4	1.0	10
Oxalic acid II	−17.8 ± 0.1	−17.9[#]	1.0	22

[#]For traceability, $\delta^{13}C$ is normalized to the reference value (Wacker et al. 2010a).

quantified using C4 and C5 wood as a modern carbon contribution of 0.9 µg with an uncertainty of 33%. Measurement results are presented in Table 2. Repetitions of the same sample produced data that are statistically indistinguishable within measurement uncertainties. The dendrochronological age of the wood was converted to ^{14}C age and its uncertainty using the IntCal09 data set (Reimer et al. 2009). Comparison of the measured and the reference age matched within 95% confidence for all 20 individual determinations as well as for the means of each wood sample. The average age offset between the expected and measured ^{14}C age results in +7 ± 14 yr, i.e. with measured values older than expected on average. The reason for this small offset is unclear. A positive offset with even larger extent (25–40 yr) was also observed earlier at ETH using the BABAB method for cellulose extraction and AMS measurement with a MICADAS (Güttler et al. 2013). Although the methods used here are identical to the earlier study, we emphasize that both investigations were performed in different labs using different chemicals, materials, and batches of standards and that the ^{14}C analyses were conducted on different MICADAS systems. As the age offset of +7 ± 14 yr is statistically not significant, it will not be applied in future ^{14}C dating of wood.

Table 2 Radiocarbon analysis (average measured ^{14}C age from *n* determinations) of wood samples, which comprised 10 annual rings each and were dated with dendrochronology. The expected ^{14}C age and its uncertainty were determined from the wood age using the IntCal09 data set.

Sample code	Wood age [cal yr BP]	Expected ^{14}C age [yr BP]	Av. measured ^{14}C age [yr BP]	*n*
BE-1327	471–481	376 ± 12	401 ± 16	3
BE-1311	2034–2044	2076 ± 13	2078 ± 16	3
BE-1326	2185–2195	2229 ± 14	2234 ± 16	3
BE-1331	2653–2663	2455 ± 13	2482 ± 17	3
BE-1332	4480–4490	4003 ± 13	3998 ± 17	3
BE-1329	5109–5119	4488 ± 13	4478 ± 19	2
BE-1328	9650–9660	8700 ± 18	8713 ± 20	3

There has been a 15-yr-long collaboration between University of Bern and ETH Zürich on the ^{14}C analysis of small samples. Joint projects covered development of the gas ion source and the gas inlet system (Ruff et al. 2007; Wacker et al. 2013a), coupling of an elemental analyzer and other combustion instruments with the AMS (Perron et al. 2010; Ruff et al. 2010), development of sample pretreatment methods and instrumentation for routine ^{14}C dating (Němec et al. 2010ab; Wacker et al. 2010b) and applications to carbonaceous aerosols in the atmosphere and in glacier ice (Sigl et al. 2009; Szidat 2009a,b; Zhang et al. 2012). About >2000 unknown gas samples were measured within these projects at the ETH AMS systems until the end of 2012. During the first 8 months of 2013,

already >400 unknown gas samples with carbon masses down to <3 µg have been analyzed with the new MICADAS based on the techniques shown in Wacker et al. (2013a).

CONCLUSION AND OUTLOOK

The new Bern Laboratory for the Analysis of Radiocarbon with AMS (LARA) is equipped with a MICADAS and dedicated sample preparation instrumentation including an automated graphitization equipment (AGE). A gas interface allows the transfer of CO_2 to the gas ion source of the MICADAS from sealed glass ampoules and combustion or acidification devices for on-line analysis of small samples. Quality assurance analyses of IAEA standards, which were processed by combustion and graphitization, revealed good agreement between measured and reference values as well as a detection limit of ~52 kyr BP. ^{14}C measurements of wood after cellulose extraction also matched well with dendrochronological dates with a non-significant average age offset of +7 ± 14 yr towards older ages. Further quality assurance measures are currently undertaken or designated, e.g. on macrofossils, bulk sediment, atmospheric CO_2, carbonates, charcoals, and bones.

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