

ONLINE ^{13}C AND ^{14}C GAS MEASUREMENTS BY EA-IRMS–AMS AT ETH ZÜRICH

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ABSTRACT. Studies using carbon isotopes to understand the global carbon cycle are critical to identify and quantify sources, sinks, and processes and how humans may impact them. ^{13}C and ^{14}C are routinely measured individually; however, there is a need to develop instrumentation that can perform concurrent online analyses that can generate rich data sets conveniently and efficiently. To satisfy these requirements, we coupled an elemental analyzer to a stable isotope mass spectrometer and an accelerator mass spectrometer system fitted with a gas ion source. We first tested the system with standard materials and then reanalyzed a sediment core from the Bay of Bengal that had been analyzed for ^{14}C by conventional methods. The system was able to produce $\%C$, ^{13}C , and ^{14}C data that were accurate and precise, and suitable for the purposes of our biogeochemistry group. The system was compact and convenient and is appropriate for use in a range of fields of research.

KEYWORDS: ^{13}C , ^{14}C , AMS, IRMS, elemental analyzer.

INTRODUCTION

Paired ^{13}C and ^{14}C measurements have become an essential part of a tiered, integrated, analytical methodology for biogeoscience and global carbon cycle studies. Stable $^{13}\text{C}/^{12}\text{C}$ isotope ratios are typically used to discriminate between sources such as marine and terrestrial plant carbon, while $^{14}\text{C}/^{12}\text{C}$ ratios add temporal and apportionment capabilities through the radioactive decay of ^{14}C (Hedges et al. 1997; Megens et al. 2001; Reddy et al. 2002). With a half-life of 5730 yr, ^{14}C is particularly useful for studies concerning Earth's recent history during the Holocene. Recent studies utilizing carbon isotopes have been able to identify and quantify crucial carbon cycle processes such as the transfer of terrestrial carbon to the ocean and its burial (Vonk et al. 2014; Mann et al. 2015; Tao et al. 2015). This has led to significant improvements in our understanding of the Earth's natural processes and the impact of humans.

The measurement of ^{13}C and ^{14}C individually is now routine and established. Stable isotope ratio mass spectrometers (IRMS) can measure $^{13}\text{C}/^{12}\text{C}$ ratios to better than 0.1‰ precision, which is sufficient for biogeochemical samples that typically span a range of 60‰ with respect to their deviation from the Pee Dee Belemnite standard ($\delta^{13}\text{C}$ VPDB) (Polissar et al. 2009). The abundance of ^{14}C is, however, only one part in a trillion and therefore requires an accelerator mass spectrometer (AMS) to achieve the required overall system efficiency and the elimination of isobars and interferences such as ^{14}N and ^{13}CH (Synal et al. 2007). Measurement of $^{14}\text{C}/^{12}\text{C}$ ratios typically spans a range from modern atmospheric levels to ancient ^{14}C -free samples corresponding to a fraction modern ($F^{14}\text{C}$) from 1 to 0. A precision of $\pm 2\%$ is routinely achievable for the modern standard oxalic acid II (NIST SRM 4990C) and the detection limit is typically less than $F^{14}\text{C}$ 0.002 (52 ka BP). The technique is now readily accessible to scientists; however, it is still comparatively intensive with respect to cost and instrumentation (Wacker et al. 2010b, 2010c).

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At this point, it is important to highlight that in an AMS laboratory the ^{13}C content of a sample is additionally used as a correction parameter for the ^{14}C content (Donahue et al. 1990; Reimer et al. 2004). This is an important concept whereby the isotopic fractionation of ^{14}C from natural processes occurs at a rate approximately twofold that of ^{13}C and that fractionation must be corrected for so that ^{14}C can be used on a uniform timescale.

Due to the design of sputter ion sources, AMS systems are not as precise as IRMS systems; thus, ^{13}C measurements for the sample ^{13}C and ^{14}C corrections are typically made on separate systems. In some laboratories, offline IRMS sample $\delta^{13}\text{C}$ is used for retroactive ^{14}C correction calculations; however, where possible, it is considered preferable to use concurrent $^{13}\text{C}/^{12}\text{C}$ data obtained from the AMS during measurement since part of the fractionation that has to be corrected for is induced in the sputter ion source itself (Santos et al. 2007; Prasad et al. 2013). Due to the reasons outlined above, the arrangement of instrumentation in AMS laboratories can occur in several ways.

Conventional AMS measurements use samples prepared as solid graphite and a cesium sputter ion source to produce high-intensity carbon ion beams. To convert non-gaseous samples to graphite, they are first converted to CO_2 by combustion or acid decomposition and subsequently reduced with hydrogen over an Fe catalyst (Vogel et al. 1984). A portion of the CO_2 gas can be diverted and measured using an IRMS for a high-precision $\delta^{13}\text{C}$ measurement with the remainder of the sample graphitized. The ^{13}C content of the graphite can then be measured by the AMS system and used for fractionation correction purposes. Hence, we find laboratories that have IRMS systems integrated online and offline with their graphitization systems (Gagnon et al. 2000; Hong et al. 2010; Kato et al. 2014).

AMS systems can also be fitted with a gas ion source whereby the samples are introduced directly as CO_2 gas as an alternate mode of operation (Bronk Ramsey et al. 2004; Fahrni et al. 2013). Here it is possible to analyze small samples, but, due to reduced system efficiencies, the measurement precision is typically reduced to 1% or better for a modern sample (Ruff et al. 2010a). The advantage, however, is that direct coupling of interfaces such as an elemental analyzer (EA) and/or an IRMS is possible, which can improve productivity where moderate-precision ^{14}C measurements are acceptable (Ruff et al. 2010b; Wacker et al. 2013; Braione et al. 2015; Salazar et al. 2015). This fits well with biogeochemical studies that seek to understand global processes and have large sample sets requiring high-precision ^{13}C and moderate-precision ^{14}C data.

In this study, we outline the features of our integrated, online, gas-accepting ion source, EA-IRMS-AMS system in routine use at ETH Zürich. For sediment and soil samples from the biogeochemistry group, we have moved away from graphite preparation and separate IRMS and AMS measurement to routine online measurements that are adequately precise for the group's studies and goals. Our first goal was to construct a high-performance, compact, automated system to increase productivity and convenience. The second goal was to be able to analyze 20 mg of Holocene sediment or soil containing typically 1 wt% organic carbon for $\delta^{13}\text{C}$ with precision of better than $\pm 0.1\%$ VPDB and F^{14}C with a precision of better than $\pm 1\%$.

EXPERIMENTAL

System Description

The system is comprised of an elemental analyzer (vario MICRO cube, Elementar) and a stable isotope ratio mass spectrometer (visION, Isoprime) connected to a gas interface system (GIS,

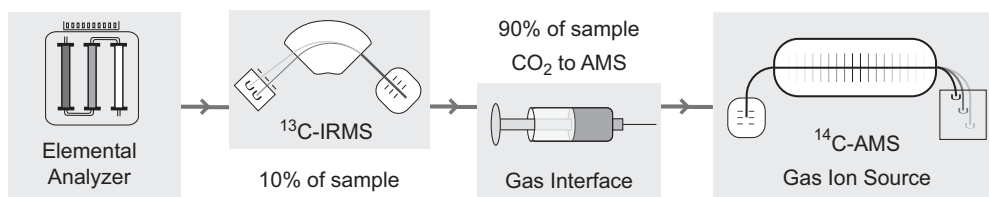


Figure 1 Schematic of the EA-IRMS-AMS system for online paired ^{13}C and ^{14}C gas measurements. Samples are combusted in an elemental analyzer (EA) and the product CO_2 is transferred to a stable isotope ratio mass spectrometer (IRMS) for high-precision ^{13}C measurement; 90% of the gas is split internally by the IRMS and sent to the accelerator mass spectrometer system (AMS) for ^{14}C measurement. Details of the gas interface system and EA-IRMS can be found in Ruff et al. (2010a, 2010b).

Ionplus) and a Mini Carbon Dating System (MICADAS, Ionplus) (Figure 1). Connecting tubing was 1/16" stainless steel and additional 4-port and 6-port switching valves were used to provide multiple modes of operation between the various interfaces and mass spectrometers (Figure S1, online Supplementary Material). This way, for example, the EA-IRMS system could be used standalone while the AMS was being used with a carbonate handling system (CHS, Ionplus) or an ampoule cracker. The footprint of the interfaces was 2 m \times 1 m and fitted alongside the MICADAS system.

The IRMS we selected has an internal backpressure controller that is used to split the flow from the EA between the IRMS source and IRMS vent. The vent of the IRMS was connected to the GIS and the backpressure controller set such that 10% of the gas flowing from the EA went to the ion source of the IRMS and the remaining 90% was trapped for AMS analysis. The backpressure controller provided the additional benefit of maintaining a constant pressure of gas to the IRMS while the GIS trap was actuating and heating.

Calibration of Standards

The standards selected for EA-IRMS-AMS were oxalic acid II (NIST SRM 4990C), phthalic anhydride (Sigma, PN-320064-500g, LN-MKBH1376V), atropine (Säntis, PN - SA990746B, LN- 51112), and acetanilide (Merck, PN-100011, LN -K37102211229). For each, $500 \pm 50 \mu\text{g C}$ were loaded into 5 \times 8 mm tin foil capsules (Säntis) and analyzed by conventional EA-IRMS for $\delta^{13}\text{C}$ VPDB against the primary standards IAEA-CH3, IAEA-CH7, and IAEA-CH6. Atropine and acetanilide are additionally elemental analysis standards while oxalic acid and phthalic anhydride are ^{14}C isotope standards.

The EA was operated in CN analysis mode with the method modified to include an additional column burn-off step at the end of the analysis where the internal gas adsorption column used for separating CO_2 and N_2 column is heated to 200°C before cooling to 50°C. Quartz tubes of 25 mm were used with the CuO combustion tube set to 920°C and the Cu reduction tube at 550°C. The combustion tube was packed with 5-mm quartz wool, 10-mm quartz chips, 5-mm quartz wool, 50-mm silver wool, 5-mm quartz wool, 65-mm CuO wire, and 3-mm corundum balls. Al_2O_3 wool was used in the ash finger. Standards were combusted using an 80-s injection of supplementary oxygen at 30 mL/min. The elemental data were processed separately using the vario MICRO software.

The IRMS method was a standard CN method modified to monitor carbon only with monitoring gas injected for 2 \times 30 s before and after the CO_2 peak of interest. Data were processed separately using the IonOS software.

EA-IRMS–AMS Analysis of Standards

Eight replicates of 50–150 $\mu\text{g C}$ of oxalic acid II, phthalic anhydride, acetanilide, atropine, IAEA-C6, and IAEA-C8 were weighed into tin foil capsules. They were run in order sorted firstly from blank to modern and secondly from large to small. Three additional phthalic anhydride blanks were run at the end after the IAEA-C6 to assess system memory. The IRMS was operated in a standalone mode with the method based on timed events and a single start trigger inputted from GIS software.

The AMS was run in gas mode and configured to run with the EA and GIS using a method modified to incorporate the IRMS (Ruff et al. 2010b; Fahrni et al. 2013). The timing schedule begins with the start trigger sent to EA and IRMS and had a total runtime of 15.5 min per sample, which gave a precision of <1% on a single oxalic acid standard. The zeolite trap of the GIS was cooled to 10°C for trapping and heated to 450°C for desorption. Data were processed separately using BATS software (Wacker et al. 2010a) and oxalic acid (NIST SRM4990C) and phthalic anhydride were used for calibration of both ^{13}C and ^{14}C data.

EA-IRMS–AMS Analysis of a Sediment Core

The sediment core NGHP-01-16A was collected from the Bay of Bengal in 2006 as part of the Indian National Gas Hydrate Program (Collett et al. 2014) and ^{14}C analysis of foraminifera has been previously conducted (Ponton et al. 2012). The core was stored frozen at the Woods Hole Oceanographic Institution and subsampled at 3-cm intervals from 20 to 750 cm. Samples were packed in dry ice and shipped to ETH Zürich where they were fumigated in $8 \times 8 \times 15$ mm silver boats (Elementar) with HCl to remove carbonate (Komada et al. 2008) and neutralized for 24 hr at 60°C over solid NaOH to remove residual acid. The samples were wrapped in a second $8 \times 8 \times 15$ mm tinfoil boat (Elementar) and pressed prior to analysis.

Fumigated samples were analyzed for ^{14}C via conventional solid graphite. Graphite samples containing 1 mg C were prepared using an AGE 3 system (Ionplus) and analyzed using a MICADAS system (Ionplus). Samples were normalized using oxalic acid II (NIST SRM4990C) and anthracite coal as a blank. Secondary standards were IAEA-C7 and -C8. Data were processed using BATS software (Wacker et al. 2010a).

Samples were then run as gas and were prepared to contain 200–500 $\mu\text{g C}$. The samples were split into groups of 17 and bracketed by 200- $\mu\text{g C}$ standards and blanks. We began and finished the run with oxalic acid and phthalic anhydride and separated the groups with three oxalic acids and one atropine. The runtime was shortened to 13.6 min and the standards were combusted in the EA with 80 s of supplementary oxygen while the samples had 120 s. The GIS has a capacity of 100 $\mu\text{g C}$ and auto-split mode is used to reduce the size of the sample before dilution and injection into the AMS.

RESULTS AND DISCUSSION

Calibration of Standards

The results of the calibration of the standards for $\delta^{13}\text{C}$ VPDB using the standalone EA-IRMS system are given in Table S1 in the online Supplementary Material. No significant drift was observed; however, we used a multipoint correction for offset (Coplen et al. 2006). The results show that the IRMS is able to measure standards to a precision of 0.05‰ or better for $n = 4$ –8. This is more than sufficient for the specification of our group of 0.1‰ and $n = 4$ –8 standards are suitable for a typical AMS run. The value we determined for oxalic acid II

was $-17.69 \pm 0.03\%$, which fell within error of the high-precision IRMS value report by Schneider et al. (1995) of $-17.68 \pm 0.02\%$. Our value is higher than the consensus value used by AMS laboratories of -17.8% ; however, it is well within the range of values reported by Mann (1983) that were used to determine the consensus value. We have adopted the more precise IRMS value of Schneider et al. (1995) for use in our laboratory. By calibrating these materials, we have a robust set of standards that can be used to collect $\%C$, $\%N$, C/N , ^{13}C , and ^{14}C data depending on the requirements of the analysis.

EA-IRMS-AMS Analysis of Standards

The results of the analysis of standards by EA-IRMS-AMS are given in Table 1. The results presented here are from the first run of the system. Again, the standards were measured precisely for ^{13}C and all of them fell within error of the consensus values at the 2σ level. Atropine was anomalously lower than the consensus value in this run and we were unable to explain this atypical result or improve it by performing the offset correction with additional standards.

We observed no crosstalk or systematic shifts in the acquired ^{13}C ratios based on the mass of the sample, which showed the IRMS system could be operated with samples containing as little as $50\ \mu\text{g C}$. The EA-AMS system has been characterized for operation down to $5\ \mu\text{g C}$, and preliminary IRMS tests indicate it can be operated between $5\text{--}50\ \mu\text{g C}$ with data correction (data not shown). Between 5 and $50\ \mu\text{g C}$ is the range at which extraneous carbon begins to have a noticeable effect and requires correction for constant contamination and crosstalk (Shah and Pearson 2007; Ruff et al. 2010b; Santos et al. 2010; Salazar et al. 2015).

Similarly, the ^{14}C data for the acetanilide, atropine, IAEA-C8, and IAEA-C6 was within error of the consensus values at the 1σ level. The oxalic acid standards were each measured to 8% , producing a mean value with 3% precision ($n = 8$) and a scatter of 2% . The blank value was typical for this system and corresponded to background of $F^{14}\text{C}$ 0.0046 ± 0.0012 (43 ka BP). System blanks are dependent on the carbon content of the EA capsules used, memory, crosstalk, and ion source cleanliness. The data for the standards were corrected for a constant contamination of $0.5\ \mu\text{g C}$ with a $F^{14}\text{C}$ of 0.6 , which is typical for the capsules we use (Ruff et al. 2010b).

In this analysis, we ran three additional blanks after the eight replicates of IAEA-C6 to study an extreme case of crosstalk. The $F^{14}\text{C}$ decreased sequentially from 0.0133 to 0.0065 and then 0.0042 and shows what we typically experience, which is that the EA and GIS system shows $<1\%$ crosstalk and that we can return to background levels after two samples. Crosstalk in interfaces is unavoidable and we have mitigation procedures to minimize this limitation. The choice of capsule size and material has been shown to have a first-order effect (Ruff et al. 2010b), and after that we consider the running order of samples and the preparation methods. The calibration and tuning procedure starts with oxalic acid followed by blanks until stable values are obtained, then samples are run in order from ancient to modern to minimize the crosstalk. Preconditioning steps such as EA and trap “burn off” have been used in EA-AMS systems (Salazar et al. 2015) and unknown samples could easily be rerun during the sequence. In this way, we can minimize or omit the application of correction procedures for subtracting crosstalk from previous samples. Development is ongoing to reduce the crosstalk in the GIS system.

EA-IRMS-AMS Analysis of a Sediment Core

The results from the EA-IRMS-AMS analysis of the Bay of Bengal core are shown in Figures 2, 3, and 4. Fully detailed data will be presented and interpreted in a future thesis and publication. The samples analyzed fall within the working range of the EA ($0\text{--}3\ \text{mg C}$) and of the IRMS

Table 1 Analysis of standards by EA-IRMS–AMS. Oxalic acid and phthalic anhydride are calibration standards for both ^{13}C and ^{14}C .

Standard	<i>n</i>	Mass range ($\mu\text{g C}$)	Mean $^{12}\text{C}^+$ (μA)	^{14}C consensus (Fm $\pm 1\sigma$)	^{14}C measured (Fm $\pm 1\sigma$)	$\delta^{13}\text{C}$ consensus ($\text{‰} \pm 1\sigma$)	$\delta^{13}\text{C}$ by IRMS ($\text{‰} \pm 1\sigma$)	$\delta^{13}\text{C}$ by AMS ($\text{‰} \pm 1\sigma$)
Phthalic anhydride	6	84–100	7.8	Blank ^b	0.0046 ± 0.0012	$-30.01 \pm 0.01^{\text{d}}$	-30.01 ± 0.03	-27.99 ± 2.5
Acetanilide ^a	6	104–166	7.8	0.0012 ± 0.0004	0.0023 ± 0.0014	$-27.58 \pm 0.02^{\text{d}}$	-27.57 ± 0.05	-23.65 ± 0.88
Atropine ^a	8	80–147	7.6	0.4337 ± 0.0025	0.4302 ± 0.0051	$-21.43 \pm 0.01^{\text{d}}$	-21.15 ± 0.13	-16.00 ± 2.11
IAEA-C8	8	54–83	7.5	0.1503 ± 0.0017	0.1499 ± 0.0029	-18.31 ± 0.11	-18.32 ± 0.06	-14.66 ± 1.34
Oxalic acid	8	76–107	7.7	1.3407^{c}	—	$-17.68 \pm 0.02^{\text{e}}$	-17.68 ± 0.06	-17.8 ± 2.9
IAEA-C6	8	73–130	8.0	1.5061 ± 0.0011	1.5084 ± 0.0116	$-10.45 \pm 0.03^{\text{f}}$	-10.50 ± 0.02	-12.17 ± 2.24

^aIn-house standard; ^bFor ^{14}C blank subtraction; ^cFor ^{14}C normalization; ^dThis study; ^eFrom Schnieder et al. (1995: 693); ^fFrom IAEA-CH6.

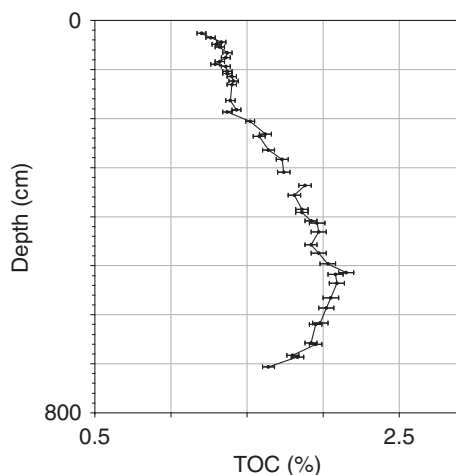


Figure 2 Plot of total organic carbon (TOC) vs. depth as determined by EA-IRMS-AMS for sediment samples taken from a core from the Bay of Bengal. The relative error based on $n = 16$ oxalic acid standards was 2%.

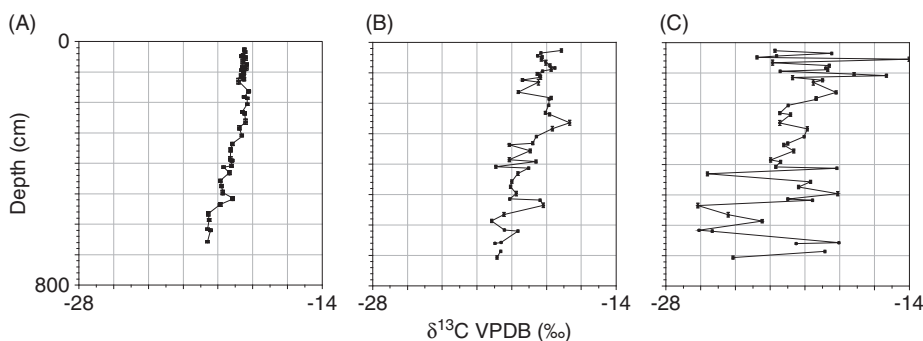


Figure 3 ^{13}C analysis by EA-IRMS-AMS of sediment samples from a core from the Bay of Bengal: (A) IRMS data with a precision of $<0.1\text{‰}$; (B) AMS graphite data; (C) AMS gas data using a gas ion source.

(200–700 $\mu\text{g C}$) for high-precision measurements. Comparison of the EA and GIS data showed that 90% of the sample CO_2 generated by the EA was trapped by the GIS. This was equal to the split ratio of the IRMS and indicates that the GIS was able to trap all of the CO_2 gas delivered to it from the IRMS for sample sizes up to 470 $\mu\text{g C}$. The GIS, however, is typically operated at a 100 $\mu\text{g C}$ capacity (at 4% CO_2 in helium), so it automatically reduces the quantity of the trapped CO_2 to 100 $\mu\text{g C}$ prior to dilution with He and injection into the AMS. Any isotopic fractionation of the CO_2 occurring during the trapping and splitting steps is corrected for by the AMS ^{13}C measurement and fractionation correction in ^{14}C data reduction (Donahue et al. 1990).

Using the EA, it is possible to obtain %C, %N, and C/N during analysis; however, in this study we only collected data for %C. By incorporating a secondary standard such as atropine into the run, we have additional calibration points for elemental analysis and ^{13}C . The precision of the %C measurements was 2% RSD based on $n = 16$ oxalic acid standards, which is more than sufficient for our requirements. Normally, unless prior knowledge of the %C content of the

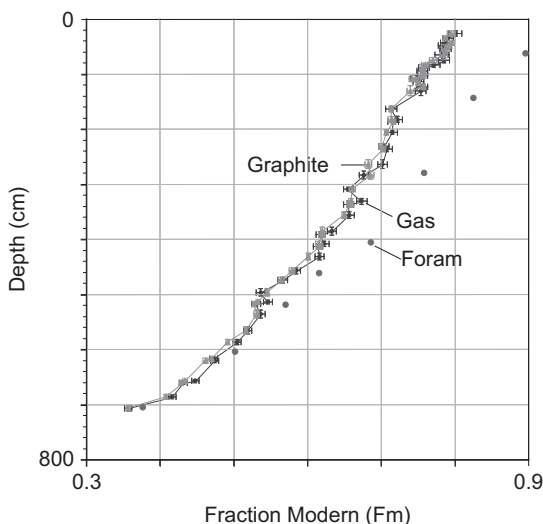


Figure 4 ^{14}C analysis by EA-IRMS-AMS of sediment samples from a core from the Bay of Bengal. Green triangles are conventional solid graphite data and blue circles are data from CO_2 using a gas ion source. Data from 46/47 gas samples are within error of the graphite samples at the 2σ level. The single missing data point was due to a bad cathode. For comparison, red squares are conventional graphite ^{14}C values for foraminifera from Ponton et al. (2012).

samples is available, we perform an initial screening run with the EA so that we can set the size of the samples to fit within the working range of the system. An additional limitation of this study was that the IRMS system was not configured for autodilution of the samples. As a result, the sample sizes needed to be within a relatively narrow carbon range, and we could not capture ^{15}N for these sediment samples, which had a relatively low N content.

The data for ^{13}C content are clearly superior from the IRMS and the precision was 0.1‰ for oxalic acid ($n = 21$), 0.06‰ for phthalic anhydride ($n = 13$), and 0.09‰ for atropine ($n = 6$) (Figure 3). The results show that as little as $n = 6$ standards can be used; however, we include more so that we can monitor drift in the IRMS and AMS systems. In Figure 3, we additionally show data for ^{13}C acquired by the AMS during graphite (B) and gas (C) analysis. The data are sample-averaged and are used for the instantaneous online correction of the ^{14}C data. The scatter of the data shows that it is not reliable for use as the accurate $\delta^{13}\text{C}$ VPDB of the sample. This highlights the importance of obtaining a separate stable isotope measurement by IRMS for this purpose. It should be noted, however, that these data are acquired using the prototype MICADAS system and that the latest MICADAS systems are capable of obtaining better quality ^{13}C data.

The data for the ^{14}C content showed that 46/47 of the samples analyzed using solid graphite and CO_2 gas fall with error of each other at the 2σ level, confirming that the gas ion source can be used to generate accurate data (Figure 4). This core has previously been analyzed for foraminiferal ^{14}C and the ages from 11 carbonate samples were younger by up to a thousand years. The shift is consistent for the different sources of the samples (organic vs. inorganic C) and will be interpreted in a future publication; nonetheless, the foraminifera data support the ages found in this study. In this run, the precision and scatter of the oxalic acid standards was 2‰ and the

precision of the samples was 10‰. In these samples, there was enough carbon to double the measurement time and precision; however, we accepted the shorter runtime preferentially. The precision and blank of the graphite data were 5‰ and $F^{14}\text{C}$ 0.006 (40 ka BP), and for the gas were 10‰ and $F^{14}\text{C}$ 0.015 (33 ka BP). The background was elevated in the gas run, as the ion source required cleaning.

The accuracy of the gas data could be further improved by applying a correction for an assumed constant contamination and crosstalk; however, we did not run processing controls in this batch and can only perform a speculative correction. The gas and graphite data show the best match when a correction for constant contamination of 6 $\mu\text{g C}$ with a $F^{14}\text{C}$ of 0.9 is performed. This mass and $F^{14}\text{C}$ is considered moderately high but not unreasonable for the large tin boats and fumigation procedure we use. A consequence of the correction is that the error is approximately doubled for the gas samples due to the propagation of the errors and the larger influence on and smaller sample sizes. In order for the corrections to be applied rigorously, processing controls must be run with each batch of samples.

Practical Aspects to Operation of the System

The primary advantage of the system was its integration, flexibility, and throughput. The ability to operate the system in several modes either as the full EA-IRMS-AMS system or as independent systems, such as CHS-AMS and EA-IRMS, standalone EA, and standalone AMS with ampoule cracker, meant that capacity wastage was minimized. In full system mode, it is possible to run continuously with the only intervention required being changing the cathode magazine every 40 cathodes and performing EA maintenance. EA maintenance to change the ash finger or reduction tube could be done in less than 10 min with the IRMS and AMS paused. We were able to routinely run batches of more than 50 samples overnight with the main limitation being staff hours. It is worth noting that the startup of the full system was relatively time consuming due to the use of four individual components (EA, IRMS, GIS, AMS) and was not practical for small batches.

CONCLUSIONS

The EA-IRMS-AMS system described in this paper was able to meet the specified requirements for the analysis of soils and sediments in our biogeochemistry group. The system was able to analyze 20 mg of modern sediment or soil containing 1 wt% organic carbon for $\delta^{13}\text{C}$ with precision of better than $\pm 0.1\text{‰}$ and ^{14}C with an $F^{14}\text{C}$ precision of better than $\pm 1\%$. It was additionally able to obtain % organic carbon with an RSD of 2%. The system was also capable of analyzing samples containing less than 100 $\mu\text{g C}$, although further validation experiments are required for small samples containing 5–100 $\mu\text{g C}$. Careful analysis of processing controls are required to quantify the addition of extraneous carbon and to correct for constant contamination and crosstalk. The system has been able to increase the productivity of our group and has allowed us to move away from conventional preparation of graphite for these types of samples. The system is a high-performance, compact, automated (with supervision) system that would be suitable for use in other fields such as archaeology, paleoclimatology, soil science, biomedicine, and forensics.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <http://dx.doi.org/10.1017/RDC.2016.68>.

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