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October 18, 2006

Radiocarbon

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Methods for high precision ^{14}C AMS measurement of atmospheric CO_2 at LLNL

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ABSTRACT

Development of ^{14}C analysis with precision better than 2 ‰ has the potential to expand the utility of $^{14}\text{CO}_2$ measurements for carbon cycle investigations as atmospheric gradients currently approach traditional measurement precision of 2-5 ‰. The AMS facility at the Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, produces high and stable beam currents that enable efficient acquisition times for large numbers of ^{14}C counts. One million ^{14}C atoms can be detected in approximately 25 minutes, suggesting that near 1 ‰ counting precision is economically feasible at LLNL. The overall uncertainty in measured values is ultimately determined by the variation between measured ratios in several sputtering periods of the same sample and by the reproducibility of replicate samples. Experiments on the collection of one million counts on replicate samples of CO_2 extracted from a whole air cylinder show a standard deviation of 1.7 ‰ in 36 samples measured over several wheels. This precision may be limited by the reproducibility of Oxalic Acid I standard samples, which is considerably poorer. We outline the procedures for high-precision sample handling and analysis that have enabled reproducibility in the cylinder extraction samples at the <2 ‰ level and describe future directions to continue increasing measurement precision at LLNL.

INTRODUCTION

Monitoring of atmospheric $^{14}\text{CO}_2$ has been conducted for over five decades using counting methods (e.g. Levin et al. 1985, Nydal and Lovseth 1983, Manning et al. 1990, Levin and Kromer 2004) and more recently, by accelerator mass spectrometry (AMS) (Meijer et al. 2006, Turnbull et al. 2006, Kim Currie personal communication). These analyses captured significant variability between many tropospheric sampling sites following the nuclear weapons tests; yet few of these sites have continued consistent measurements and recent observations show regional and seasonal gradients that are quite small (Levin and Hesshaimer 2000, Levin and Kromer 2004). Continued observation of atmospheric $^{14}\text{CO}_2$ has the potential to be an important tool in global and regional carbon cycle studies because different sources of CO_2 have distinct $^{14}\text{CO}_2$ signatures (Levin and Hesshaimer 2000). We are developing improved methods of CO_2 sample handling and AMS analysis in order to enhance the ability to resolve small changes in $\Delta^{14}\text{CO}_2$ and thereby, expand the use of ^{14}C for identifying and quantifying carbon fluxes.

Achieving Poisson counting uncertainty near 1 ‰ increases the required AMS analysis time by a factor of four compared to a traditional counting uncertainty of 2 ‰. Rapid ^{14}C detection rates are necessary to reduce the cost of such high precision analyses. The HVEC FN Tandem accelerator facility at the Center for AMS (CAMS), Lawrence Livermore National Laboratory (Davis 1989, Davis et al 1990), is capable of count rates between 500 – 1000 counts per second for modern samples of 0.4-1 mg C. This is

accomplished through a high efficiency cesium sputter ion source (~35% C⁻ production efficiency) and wide-open beam transport that essentially eliminates beam losses (Southon and Roberts 2000, Fallon et al. 2006). A preliminary study at LLNL in 2003 collected near 1 million ¹⁴C counts on samples of oceanic dissolved inorganic carbon that were split into 2 targets for analysis, generally showing better than 1 ‰ agreement on 33 pairs of targets ranging in value from ~0 ‰ to -240 ‰ (Guilderson et al. 2006).

Samples of atmospheric CO₂ are excellent candidates for high precision analysis since they do not require rigorous pretreatment procedures that may introduce contamination (Bronk Ramsey et al. 2004), and the modern ¹⁴C concentrations reduce the effects of laboratory and instrument backgrounds. In addition to the counting uncertainty, uncertainties may be introduced during sampling, CO₂ extraction and graphitization. Machine instabilities and differences in the character and behavior of graphite targets during analysis will also contribute to the AMS measurement uncertainty. These contributions can be estimated by measuring replicate samples of reference materials that undergo the same handling and analysis procedures as unknown samples. To estimate the magnitude of external uncertainty that may be added to atmospheric CO₂ samples, we utilize a new reference material for radiocarbon analysis - CO₂ gas extracted from a pressurized whole air cylinder.

Our handling and analysis procedures are being developed to measure CO₂ extracted from whole air flask samples from the Scripps Carbon Dioxide Research Group. In the Scripps laboratory, air cylinders are processed using the same cryogenic extraction system as the flask samples. We use a cylinder that was filled with dry, ambient air from the La Jolla Pier in November 2004. This cylinder has a similar CO₂ concentration and isotopic character as recent atmospheric samples (pCO₂ = 380.48 ppm, Δ¹⁴C = 61.3 ‰, δ¹³C = -8.4 ‰). We use the same air cylinder handling and extraction techniques that are employed for stable isotope analysis at Scripps. These techniques have been calibrated to 0.03 ‰ precision and accuracy in δ¹³C by long term reference materials and interlaboratory comparisons (Guenther et al. 2001). Based on the established reliability of these procedures for similar samples of δ¹³C, we assume that fractionation or contamination during extraction is negligible and that all additional uncertainty in Δ¹⁴C measurements is introduced during graphitization and analysis.

METHODS

The high precision methods used in this study have evolved over two years of development in efforts to maximize the utility of the rapid counting ability at LLNL by minimizing the uncertainty added by sample handling and analysis. We have attempted to identify various possible sources of uncertainty and introduced several improvements to the standard procedures at LLNL. The following description outlines the methods we have developed and implemented for high precision analysis.

At Scripps, CO₂ gas is extracted from whole air in a glass vacuum manifold by passing through a quartz spiral trap immersed in liquid nitrogen at 0.25 liter/min. The CO₂ sample is frozen into a Pyrex tube, which is sealed using an automated fuser system. For

these experiments, tubes containing cylinder extractions were stored in a drawer for several weeks to 18 months.

At LLNL, oxalic acid and barley mash reference materials are combusted by heating with copper oxide, following an acid-base-acid pretreatment for the barley mash. Each combustion produces 4-6 mg C, which is split into 5-12 samples of approximately 0.5 mg C, allowing 2 minutes to isotopically equilibrate and disposing of any excess CO₂.

All CO₂ samples are graphitized at LLNL in Kimax glass tube reactors by heating to 570°C in the presence of an iron catalyst and hydrogen gas (similar to Vogel et al. 1987), using magnesium perchlorate to trap the water evolved during the reduction (Santos et al. 2004). The resulting graphite-iron mixture is pressed into aluminum target holders using a sample press.

Graphite targets are placed in a sample wheel and analyzed for ratios of ¹⁴C⁴⁺-cts/¹³C⁴⁺-charge at LLNL in sets of approximately 24 targets. Each wheel typically contains 6 Oxalic Acid I targets (OXI), 2 Oxalic Acid II (OXII) targets, 2 barley mash (VIRI A) targets, 4 cylinder extraction targets (Cyl-1) and 10-12 unknown targets. Targets are sputtered in periods lasting 200 seconds or until 50,000 ¹⁴C counts are recorded in the detector. Usually, 50,000 counts are acquired in 50-90 seconds. The targets are sputtered sequentially and the wheel is cycled at least 20 times to perform 20 sputtering periods on each target. The integrated ¹⁴C-cts/¹³C-charge ratio is recorded for each sputtering period. Up to 4 additional periods may be performed on a target if the standard deviation in the target's ¹⁴C/¹³C ratios over the 20 periods exceeds 0.7%. This is usually only necessary for 1-2 targets in each wheel due to an outlier or a low ratio in the first one or two sputtering periods as the target is warming up. A standard deviation of 0.7% in the ¹⁴C/¹³C ratios of Cyl-1 translates to a standard error of 1.0-1.5 ‰ in Δ¹⁴C after normalization to OX1. Because of daily instrument fluctuations, ratios in all samples are observed to drift by <1% over the ~14 hour course of measurements.

Specific changes we have made to the standard procedures at LLNL for high precision sample preparation and analysis include:

- The use of a new batch of iron catalyst that produces finer, looser graphite. This reduces the possibility of spatial inhomogeneities in the isotopic concentration of the graphite and homogenizes the graphite-iron distribution, producing more regular heating of the target in the ion source.
- The iron catalyst added to the reactors is weighed to 5.5 ± 0.2 mg instead of being approximated by a measuring spoon, providing a more consistent ratio of graphite to iron.
- Dry ice-ethanol cold traps were replaced by magnesium perchlorate in the graphitization reactors. The perchlorate provides lower water vapor pressure in the reactor and reduces the amount of dry ice exposed to the laboratory air, decreasing the ambient CO₂ concentration and increasing its Δ¹⁴C.
- Graphite samples are now compacted to the same pressure using a sample press, eliminating the differences in consistency of manually pounded graphite.

- The sputtering period limit was reduced from 75,000 to 50,000 counts per sputtering period because heating over long sputtering periods may alter the interaction of ions on or near the surface of the graphite target.
- The number of targets in each wheel was cut from 55 to 24 to decrease the total analysis time for each wheel and, thereby, reduce the amount of instrument drift experienced over the measurement of a wheel. In addition, the shorter time between sputtering periods means the target will experience smaller temperature variations during the course of the analysis.
- The individual samples of OXI are now split into approximately 0.5 mg C samples instead of 1 mg C so that they are more similar in size to the CO₂ samples.

Because of the high cost and demand of analysis time, we were unable to carry out sufficient characterization of the significance of each of these changes; however in the analyses presented here, we show that the use of these procedures resulted in a precision of better than 2 ‰ in replicate measurements of Cyl-1 targets.

After completion of AMS measurement, the recorded ¹⁴C/¹³C ratios are normalized to the primary OXI standard and converted to ¹⁴C/¹²C ratios using known δ¹³C values. For every target, the ¹⁴C/¹³C ratio acquired in each sputtering period is divided by the average OXI ¹⁴C/¹³C ratio in the 6 bracketing OXI sputtering periods. This typically includes one sputtering period from each of 6 OXI targets on the wheel. The normalized ratios in each sputtering period are averaged and converted to Δ¹⁴C, correcting for mass dependent fractionation and age (Stuiver and Polach, 1977).

The measurement uncertainty for each target is reported as the larger of the counting uncertainty or the standard error of the normalized ratios for all sputtering periods. The counting uncertainty is calculated as the Poisson uncertainty in the total number of ¹⁴C atoms detected in all sputtering periods of that target: 1/√n. Usually the standard error of the normalized ratios is slightly higher than the counting uncertainty. The average single target measurement uncertainty for Cyl-1 targets in this study was 1.2 ‰; we will refer to this as the internal uncertainty, σ_{Int} = 1.2 ‰.

DISCUSSION

Another estimate of the measurement uncertainty of Δ¹⁴C in CO₂ samples can be obtained by examining replicate measurements of Cyl-1 targets. The scatter in Δ¹⁴C of several Cyl-1 targets within one wheel incorporates the uncertainty due to graphitization and the differences in behavior of individual targets during analysis. Scatter observed between wheels reflects uncertainty due to graphitization, wheel-to-wheel differences in individual target behavior or detection efficiency, and differences in the relative ¹⁴C/¹³C ratios between different wheels' ensembles of OXI and Cyl-1 targets. Since the Δ¹⁴C values of the OXI and Cyl-1 reference materials differ by only 30 ‰, we don't expect nonlinearities in analysis to be significant.

Assuming the total uncertainty, σ_{Tot}, is a quadrature addition of independent contributions (Ellison et al. 2000), we can estimate the within-wheel contribution of uncertainty, σ_{1W}, and the between-wheel contribution of uncertainty, σ_{BW}, added to the internal

uncertainty, σ_{Int} , in measurements of $\Delta^{14}\text{C}$ in Cyl-1 (Equation 1). We measured 36 Cyl-1 targets in ten wheels, with 2-5 Cyl-1 targets on each wheel. The number of Cyl-1 targets and the mean and standard deviation of $\Delta^{14}\text{C}$ in Cyl-1 targets from each wheel and in all Cyl-1 targets are shown in Table 1.

(1) 

First, we estimate σ_{IW} by assessing the within-wheel repeatability of $\Delta^{14}\text{C}$ in the Cyl-1 targets. The standard deviation of $\Delta^{14}\text{C}$ in Cyl-1 targets on a wheel ranged from 0.6 to 1.9 ‰ (Table 1). To combine the results from all wheels, we calculated the pooled standard deviation of $\Delta^{14}\text{C}$ in Cyl-1 over the ten wheels. The pooled standard deviation is 1.3 ‰, representing the total within-wheel uncertainty observed in this study. If we consider Equation 1 for Cyl-1 samples within the same wheel, then $\sigma_{\text{Tot}} = 1.3$ ‰, $\sigma_{\text{Int}} = 1.2$ ‰ and $\sigma_{\text{BW}} = 0$ ‰. Using these values to calculate σ_{IW} by Equation 1 reveals that σ_{IW} must be very small because σ_{Tot} and σ_{Int} are essentially the same. This analysis suggests that the within-wheel repeatability is the same as the internal uncertainty, and that graphitization or individual target behavior do not substantially contribute any additional uncertainty to $\Delta^{14}\text{C}$ in Cyl-1 targets measured on the same wheel, i.e. $\sigma_{\text{IW}} = 0$ ‰.

Next, we determine σ_{BW} by considering the between-wheel reproducibility of $\Delta^{14}\text{C}$ in the Cyl-1 targets. The standard deviation of $\Delta^{14}\text{C}$ measured in all 36 Cyl-1 targets was 1.7 ‰. This represents the total uncertainty characterized in this study: $\sigma_{\text{Tot}} = 1.7$ ‰. By substituting $\sigma_{\text{Tot}} = 1.7$ ‰, $\sigma_{\text{Int}} = 1.2$ ‰ and $\sigma_{\text{IW}} = 0$ ‰ in Equation 1, we calculate $\sigma_{\text{BW}} = 1.2$ ‰. This indicates that the uncertainty introduced when targets are analyzed on several wheels, σ_{BW} , is substantial and comparable in magnitude to the internal uncertainty, σ_{Int} .

Part of the added wheel-to-wheel uncertainty is due to daily variability in several components of the AMS. This includes the stability of power supplies, variations in room temperature, the level of vacuum achieved, carbon foil thickness, cesium beam intensity, etc. There may also be differences in the character of the graphite-iron mixture in targets on different wheels. These sources of variation could cause small differences in the ionization or detection efficiency of ^{14}C compared to ^{13}C that may not be accounted for by the OXI normalization procedure. Such contributions to uncertainty are difficult to diagnose other than by observing the long-term reproducibility of measurements of $\Delta^{14}\text{C}$ on replicate samples.

Another part of σ_{BW} that is easier to quantify comes from the accuracy of $^{14}\text{C}/^{13}\text{C}$ ratios in OXI targets. The reproducibility of OXI targets affects the reproducibility of Cyl-1 $\Delta^{14}\text{C}$ because measurements of $^{14}\text{C}/^{13}\text{C}$ ratios in OXI are used in the data normalization procedure. To examine the scatter of $\Delta^{14}\text{C}$ in OXI targets within a wheel, we reversed the normalization procedure and used Cyl-1 as the primary standard to calculate $\Delta^{14}\text{C}$ in OXI targets. Then, we calculated the standard deviation in $\Delta^{14}\text{C}$ in the OXI targets on each

wheel, again combining results from all wheels into a pooled standard deviation. The pooled standard deviation of $\Delta^{14}\text{C}$ in OXI targets is 2.3 ‰, considerably larger than the pooled standard deviation in Cyl-1 of 1.3 ‰.

Variability in OXI does not have a large effect on the within-wheel repeatability of Cyl-1 $\Delta^{14}\text{C}$ because a running mean is used in normalization. The running mean is calculated with the measured $^{14}\text{C}/^{13}\text{C}$ from one sputtering period of each of 6 OXI targets. It will not be biased toward any particular OXI target and will vary only randomly and with instrument drift, thus it cannot introduce a systematic error to the $\Delta^{14}\text{C}$ calculated in any particular Cyl-1 target.

On the other hand, significant wheel-to-wheel variability in the difference between the mean Cyl-1 $^{14}\text{C}/^{13}\text{C}$ ratio and the mean OXI $^{14}\text{C}/^{13}\text{C}$ ratio will increase the overall scatter in. Mean $\Delta^{14}\text{C}$ values for the Cyl-1 targets in each wheel ranged from 57.9–62.4 ‰ (Table 1), demonstrating that the relative $^{14}\text{C}/^{13}\text{C}$ ratios between the Cyl-1 targets and the OXI targets do vary substantially between wheels. Therefore, a portion of σ_{BW} may be caused by uncertainty in the mean OXI $\Delta^{14}\text{C}$ on each wheel. Uncertainty in the mean OXI $\Delta^{14}\text{C}$ can be estimated by calculating the standard error in $\Delta^{14}\text{C}$ of OXI targets from each wheel, shown in Table 1. The standard error ranged from 0.6 to 1.4 ‰ over the ten wheels analyzed, suggesting that a considerable error in the mean OXI $\Delta^{14}\text{C}$ is possible. An error in the mean OXI $\Delta^{14}\text{C}$ on a particular wheel will result in a systematic error in the $\Delta^{14}\text{C}$ of Cyl-1 targets on that wheel, which may contribute a considerable amount to σ_{BW} . Improvements in the reproducibility of OXI therefore have the potential to improve the overall precision of CO_2 measurements at LLNL.

We believe the poorer within-wheel repeatability of the OXI targets compared to the Cyl-1 targets must be due to differences in sample preparation. Since the CO_2 gas from each combustion of OXI is split into several different samples, we would expect all the samples to be homogeneous, but perhaps the splitting procedure itself affects the samples. The Oxalic Acid II and VIRI A barley mash targets, which undergo similar preparation by combustion and splitting, showed a standard deviation of 2.0 and 2.3 ‰, respectively, in $\Delta^{14}\text{C}$ of all targets over the 10 wheels. This scatter is larger than the overall standard deviation in Cyl-1 targets but similar to the pooled standard deviation of OXI targets. Though there were only 2 targets of OXII and VIRI A on each wheel, the large overall scatter supports the idea that targets prepared by splitting large combustions are statistically different from each other.

We are currently working on different OXI handling procedures, including individual 0.5 mg C sized combustions or the combustion of a very large amount of OXI that could be stored in a cylinder and used for single 0.5 mg C sized aliquots of OXI CO_2 gas. Alternatively, we are considering the use of Cyl-1 as the primary standard for high-precision analysis of CO_2 samples at LLNL.

CONCLUSIONS

High-precision AMS measurements of cylinder-extracted CO_2 samples using newly-developed methods exhibited a standard deviation of 1.7 ‰ in 36 samples measured over

10 wheels. The standard deviation observed in all samples provides a measure of the total uncertainty characterized by this study, $\sigma_{\text{Tot}} = 1.7 \text{ ‰}$. The precision of $\Delta^{14}\text{C}$ in Cyl-1 targets analyzed on one wheel was limited by internal uncertainty, $\sigma_{\text{Int}} = 1.2 \text{ ‰}$, as the within-wheel repeatability (1.3 ‰) was comparable to the internal uncertainty. However, the overall scatter demonstrated that a considerable amount of uncertainty is introduced when samples are analyzed on several wheels: $\sigma_{\text{BW}} = 1.2 \text{ ‰}$. Wheel-to-wheel contributions of uncertainty could be due to graphitization, daily instrument variation or variability in the primary OXI standard. The scatter in measurements of OXI was substantially larger than Cyl-1, suggesting improved sample handling of OXI could improve the total precision possible. This study indicates that the AMS facility at LLNL is currently capable of achieving precision better than 2 ‰ in atmospheric CO_2 samples.

FUTURE WORK

To eliminate the effect of OXI sample handling on the estimate of σ_{Tot} in the cylinder extraction targets we plan to conduct experiments using a second reference air cylinder, Cyl-2. Measuring Cyl-2 targets will allow us to normalize $^{14}\text{C}/^{13}\text{C}$ ratios in the Cyl-1 targets with another CO_2 reference material that undergoes the same sample handling procedures. We have prepared another air cylinder, and we will conduct these analyses in the next few months.

As the LLNL AMS system measures only $^{14}\text{C}^{4+}$ and $^{13}\text{C}^{4+}$ ions, we are currently unable to detect any target-to-target differences in fractionation that may occur in the ion source as the targets are sputtered, or any target-to-target differences in electron stripping efficiency inside the accelerator. The detection of $^{12}\text{C}^-$ will be implemented in the low-energy section of the AMS in the near future, and implementation of $^{12}\text{C}^{4+}$ detection in the high-energy section is possible in the next few years. Measurement of all three carbon isotopes will allow correction of fractionation inside the instrument, further improving the detection capabilities at LLNL.

ACKNOWLEDGEMENTS

This work was supported by the University of California Office of the President, the LLNL Laboratory Directed Research and Development Program (06-ERD-031), the US Department of Energy, and a NASA Earth Systems Science Graduate Research Fellowship. We thank Tom Brown for advice and discussion, Alane Bollenbacher for performing the stable isotope analyses, Paula Zermeno and Dorothy Kurdyla for assisting with graphitization, Adam Cox for preparing the air cylinders and two anonymous reviewers for improving the manuscript. A portion of this work including radiocarbon analyses were performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory (contract W-7405-Eng-48).

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Table 1. Results from 10 wheels analyzed at LLNL using high-precision methods. The mean and standard deviation in $\Delta^{14}\text{C}$ of N number of replicate Cyl-1 targets is shown for each wheel. The standard error in $\Delta^{14}\text{C}$ of replicate OXI targets is also shown for each wheel. The bottom row shows the mean and standard deviation in $\Delta^{14}\text{C}$ of all 36 Cyl-1 targets analyzed.

Wheel	N Cyl-1	Mean Cyl-1 $\Delta^{14}\text{C}$ (‰)	Standard Deviation in Cyl-1 $\Delta^{14}\text{C}$ (‰)	Standard Error in OXI $\Delta^{14}\text{C}$ (‰)
1	5	61.4	1.6	0.7
2	3	60.7	0.9	1.2
3	4	62.0	1.4	1.1
4	2	59.9	1.9	0.8
5	4	62.4	1.6	1.4
6	4	62.2	1.8	0.6
7	4	59.8	0.7	0.8
8	3	60.9	0.5	0.7
9	4	62.0	1.4	0.7
10	3	57.9	0.6	1.0
Total	36	61.3	1.7	n/a