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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 radiocarbon analysis with precision better than 2‰ has the potential to expand the utility of $^{14}CO_2$ measurements for carbon cycle investigations as atmospheric gradients currently approach the typical measurement precision of 2–5‰. The accelerator mass spectrometer at Lawrence Livermore National Laboratory (LLNL) 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 min, 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 1 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

Large amounts of radiocarbon were produced in the atmosphere during the nuclear weapons tests of the 1950s and 1960s, doubling the atmospheric inventory of $^{14}CO_2$ (Nydal and Lovseth 1983; Levin et al. 1985; Manning et al. 1990). Natural exchanges in the carbon cycle have since distributed the bomb-derived excess ^{14}C into the atmospheric, oceanic, and terrestrial carbon reservoirs. The evolution of tropospheric $\Delta^{14}C$ caused by this redistribution has been measured throughout the past 5 decades and used in many applications, including studies of atmospheric mixing, air-sea gas exchange rates, oceanic uptake of anthropogenic CO_2, and carbon turnover rates in various ecosystems (e.g. Nydal 1968; Trumbore 2000; Naegler et al. 2006). The observed atmospheric variability in $\Delta^{14}C$ of background air was initially as large as several hundred per mil following the bomb tests, but has since shrunk to only several per mil due to the large uptake of bomb-derived excess ^{14}C by the ocean and terrestrial biosphere (Nydal and Lovseth 1983; Levin et al. 1985; Manning et al. 1990; Levin and Kromer 2004; Meijer et al. 2006).

Though current gradients are small, variation in $^{14}CO_2$ still reflects carbon exchanges with the atmosphere as different sources of CO_2 have distinct ^{14}C signatures (Levin and Hesshaimer 2000). Measurements of atmospheric $\Delta^{14}C$ should continue to be an important tool in global and regional carbon cycle studies; however, their utility is limited by measurement precision. Current precision in atmospheric $^{14}CO_2$ analysis for counting and accelerator mass spectrometry (AMS) techniques at most laboratories is 2–5‰ (Levin and Kromer 2004; Meijer et al. 2006; Turnbull et al. 2006), similar to the seasonal and spatial variability in some regions. Higher-precision measurements appear to be feasible at LLNL, suggesting that it is now possible to resolve smaller changes in $\Delta^{14}CO_2$ and, thereby, expand the use of ^{14}C for identifying and quantifying carbon fluxes.

Improvement in $\Delta^{14}C$ measurement precision first requires the detection of a larger number of ^{14}C atoms to reduce the Poisson counting uncertainty ($1/\sqrt{n}$). Acquiring enough ^{14}C counts for a count-

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ing uncertainty near 1‰ increases the AMS analysis time by a factor of 4 compared to a 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 Accelerator Mass Spectrometry, 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).

Counting uncertainty is not the only factor that limits the precision attainable in ^{14}C measurements. Additional uncertainty may be introduced during sampling, CO_2 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. A preliminary study at LLNL in 2003 collected near 1 million ^{14}C counts on samples of oceanic dissolved inorganic carbon (DIC) 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). In this study, we report measurements of a new reference material for ^{14}C analysis—CO_2 gas extracted from a pressurized whole air cylinder. We estimate the total measurement uncertainty of $\Delta^{14}CO_2$ at LLNL as the standard deviation observed in 36 cylinder extraction samples measured on several wheels, and we calculate the magnitude of external uncertainty that is added during sample handling and analysis.

The methods used in this study have evolved over 2 yr in efforts to maximize the utility of the rapid counting ability at LLNL by minimizing the uncertainty added by sample handling and analysis. The difficulties faced in sample handling are smaller for modern CO_2 samples compared to carbon from other materials because the samples are already conveniently in the form of CO_2, the starting material for graphitization. This reduces the risk of errors introduced during sample pretreatment and contamination from laboratory or instrument backgrounds (Bronk Ramsey et al. 2004). Sources of uncertainty in graphitization and analysis will affect the precision attainable in CO_2 samples. We have attempted to identify and remove some of these uncertainties by introducing several improvements to the standard procedures at LLNL.

METHODS

Our handling and analysis procedures have been developed to measure CO_2 extracted from whole air flask samples from the CO_2 Program at Scripps, initiated by Charles D Keeling. The Scripps flasks are sampled by exposing 5-L evacuated glass flasks to air at one of 10 clean air sampling sites around the world. Flasks are shipped back to Scripps and measured for CO_2 concentration using a nondispersive infrared gas analyzer before the CO_2 gas is extracted.

In the Scripps laboratory, reference air cylinders and flask samples are processed using the same cryogenic extraction system. Our ^{14}C reference cylinder was filled with dry, ambient air from the Scripps Pier in La Jolla, California, in November 2004. This cylinder has a similar CO_2 concentration and isotopic character as recent atmospheric samples (pCO_2 = 380.48 ppm, $\Delta^{14}C$ = 61.3‰, $\delta^{13}C$ = –8.44‰). Extractions are performed in a glass vacuum manifold, where whole air is passed at a flow of 0.25 L/min for 10 min through a quartz spiral trap immersed in liquid nitrogen. The extracted CO_2 samples (typically 0.5 mg C) are transferred into Pyrex® tubes, which are sealed using an automated fuser system. For the analyses reported here, tubes containing cylinder extractions were stored in a drawer for several weeks to 18 months.

The same air sample and cylinder extraction techniques are employed for stable isotope analysis of CO_2 at Scripps. These techniques have been calibrated to 0.03‰ precision and accuracy in $\delta^{13}C$ by long-term reference materials and interlaboratory comparisons (Guenther et al. 2001). Based on the established reliability of these procedures for $\delta^{13}C$ analysis in similar samples, we assume that fractionation or contamination during extraction is negligible.

At LLNL, we prepare additional reference materials made of oxalic acid and barley mash. These materials are combusted to produce CO_2 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 individual samples. The CO_2 is split by expanding the gas into a larger volume, allowing 2 min to isotopically equilibrate, then taking an aliquot of approximately 0.5 mg C.

All CO_2 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 target wheel in sets of approximately 24 targets. Each wheel typically contains 6 oxalic acid I (OXI) targets, 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 of ~50–90 s, where a period lasts until 50,000 ^{14}C counts are recorded in the detector. The targets are sputtered sequentially and the wheel is cycled at least 20 times to perform 20 sputtering periods and acquire 1 million counts on each target. Ratios of $^{14}C^{4+}/^{13}C^{4+}$ are acquired by measuring $^{14}C^{4+}$ atoms reaching the detector and by measuring $^{13}C^{4+}$ as charge collected in a Faraday cup. The integrated $^{14}C/^{13}C$ 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 $^{14}C/^{13}C$ ratios over the 20 periods exceeds 0.7%. This is usually only necessary for 1 or 2 targets in each wheel due to an outlier or a low ratio in the first 1 or 2 sputtering periods as the target is warming up. A standard deviation of 0.7% in the $^{14}C/^{13}C$ ratios of Cyl-1 translates to a standard error of 1.0–1.5‰ in $\Delta^{14}C$ after averaging over 20 cycles and normalizing to OXI.

After completion of AMS measurement, the recorded $^{14}C/^{13}C$ ratios are normalized to the primary OXI standard and converted to $^{14}C/^{12}C$ ratios using known $\delta^{13}C$ values. Because of daily instrument fluctuations, ratios in all samples are observed to drift by <1% over the ~14-hr course of measurements, but the drift is largely canceled by the normalization. The normalization process is performed on every target by dividing the $^{14}C/^{13}C$ ratio acquired in each sputtering period by the average OXI $^{14}C/^{13}C$ ratio in the 6 bracketing OXI sputtering periods. This typically includes 1 sputtering period from each of 6 OXI targets on the wheel. The normalized ratios in each sputtering period are averaged and converted to $\Delta^{14}C$, 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 ^{14}C atoms detected, including a propagation of uncertainty from OXI. 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, $\sigma_{int} = 1.2‰$.

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

- Selecting a batch of iron catalyst from Alfa Aesar® that produces finer, looser graphite. The use of finer graphite reduces the possibility of spatial inhomogeneities in the isotopic concentration of the graphite and homogenizes the graphite-iron distribution in the target, producing more regular heating of the target in the ion source.
- Weighing the iron catalyst to 5.5 ± 0.3 mg to provide a more consistent ratio of graphite to iron than approximating the amount of iron with a measuring spoon (usually accurate to within 10 to 15‰.
- Replacing dry ice-isopropanol cold traps with magnesium perchlorate in the graphitization reactors. The magnesium perchlorate provides lower water vapor pressure in the reactor. In addition, the risk of contamination is reduced because less dry ice is exposed to the laboratory air, decreasing the ambient CO_2 concentration and increasing its $\Delta^{14}C$.
- Compacting graphite samples to a specified pressure using a sample press to eliminate the differences in consistency of manually pounded graphite.
- Reducing the number of targets in each wheel 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.
- Splitting the individual samples of OXI into approximately 0.5-mg C samples instead of 1 mg C so that they are more similar in size to the CO_2 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.

DISCUSSION

The internal uncertainty is one estimate of measurement uncertainty of $\Delta^{14}C$ in Cyl-1 CO_2 targets; another estimate can be obtained by examining the consistency of different Cyl-1 targets. The scatter in $\Delta^{14}C$ of several Cyl-1 targets within 1 wheel incorporates the uncertainty due to graphitization and the differences in behavior of individual targets during analysis. Scatter observed between wheels may additionally reflect wheel-to-wheel differences in individual target behavior or detection efficiency, and differences in the relative $^{14}C/^{13}C$ ratios between different wheels' ensembles of OXI and Cyl-1 targets. Since the values of the OXI and Cyl-1 reference materials differ by only 30‰ in $\Delta^{14}C$ and 11‰ in $\delta^{13}C$, we do not expect nonlinearities in analysis to be significant.

Assuming the total uncertainty, σ_{tot}, is a quadrature sum of independent contributions (Ellison et al. 2000), we can estimate the within-wheel contribution of uncertainty, σ_{IW}, and the additional between-wheel contribution of uncertainty, σ_{BW}, in measurements of $\Delta^{14}C$ in Cyl-1 according to:

$$\sigma_{tot}^2 = \sigma_{int}^2 + \sigma_{IW}^2 + \sigma_{BW}^2 \quad (1)$$

We measured 36 Cyl-1 targets in 10 wheels, with 2 to 5 Cyl-1 targets on each wheel. The number of Cyl-1 targets and the mean and standard deviation of $\Delta^{14}C$ in Cyl-1 targets from each wheel and in all Cyl-1 targets are shown in Table 1.

First, we estimate σ_{IW} by assessing the within-wheel repeatability of $\Delta^{14}C$ in the Cyl-1 targets. The standard deviation of $\Delta^{14}C$ 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 $\Delta^{14}C$ in Cyl-1 over the 10 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,

Table 1 Results from 10 wheels analyzed at LLNL using high-precision methods. The mean and standard deviation in $\Delta^{14}C$ of N number of replicate Cyl-1 targets are shown for each wheel. The standard deviation in $\Delta^{14}C$ of replicate OXI targets is also shown for each wheel. The bottom row shows the mean and standard deviation in $\Delta^{14}C$ of all 36 Cyl-1 targets and all 62 OXI targets analyzed.

Wheel	N Cyl-1	Mean Cyl-1 $\Delta^{14}C$ (‰)	Standard deviation in Cyl-1 $\Delta^{14}C$ (‰)	Standard deviation in OXI $\Delta^{14}C$ (‰)
1	5	61.4	1.6	1.5
2	3	60.7	0.9	3.0
3	4	62.0	1.4	2.7
4	2	59.9	1.9	2.0
5	4	62.4	1.6	3.6
6	4	62.2	1.8	1.5
7	4	59.8	0.7	1.9
8	3	60.9	0.5	1.8
9	4	62.0	1.4	1.8
10	3	57.9	0.6	2.3
Total	*36*	*61.3*	*1.7*	*2.4*

then σ_{tot} = 1.3‰, σ_{int} = 1.2‰, and σ_{BW} = 0‰. Using these values to calculate σ_{IW} by Equation 1 reveals that σ_{IW} must be very small (≤0.5‰) 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 $\Delta^{14}C$ in Cyl-1 targets measured on the same wheel, i.e. σ_{IW} = 0‰.

Next, we determine σ_{BW} by considering the between-wheel reproducibility of $\Delta^{14}C$ in the Cyl-1 targets. The standard deviation of $\Delta^{14}C$ measured in all 36 Cyl-1 targets is 1.7‰. This represents the total uncertainty characterized in this study: σ_{tot} = 1.7‰. By substituting σ_{tot} = 1.7‰, σ_{int} = 1.2‰, and σ_{IW} = 0‰ in Equation 1, we calculate σ_{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 σ_{BW} comes from the variability of the $^{14}C/^{13}C$ ratios in OXI targets. The reproducibility of OXI targets affects the reproducibility of Cyl-1 $\Delta^{14}C$ because measurements of $^{14}C/^{13}C$ ratios in OXI are used in the data normalization procedure. To examine the scatter of $\Delta^{14}C$ in OXI targets within a wheel, we reverse the normalization procedure and use Cyl-1 as the primary standard to calculate $\Delta^{14}C$ in OXI targets. We thus calculate the standard deviation in $\Delta^{14}C$ in the OXI targets on each wheel (shown in Table 1) and again combine the results from all wheels into a pooled standard deviation. The pooled standard deviation of $\Delta^{14}C$ in OXI targets is 2.3‰, considerably larger than the pooled standard deviation in Cyl-1 of 1.3‰. The $\Delta^{14}C$ in OXI targets also have an average internal uncertainty (σ_{int}) of 1.2‰, so for OXI targets σ_{IW} = 2.0‰, showing that a substantial amount of uncertainty is added to OXI targets analyzed on a single wheel.

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 standard deviations

of 2.0‰ and 2.3‰, respectively, in $\Delta^{14}C$ 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.

Variability in OXI does not have a large effect on the within-wheel repeatability of Cyl-1 $\Delta^{14}C$ because a running mean that typically includes all OXI targets on the wheel is used in normalization. The running mean will not be biased toward any particular OXI target and will vary only randomly and with instrument drift; thus, it tends not to introduce differences in the $\Delta^{14}C$ calculated for Cyl-1 targets on an individual wheel.

On the other hand, significant wheel-to-wheel variability in the difference between the mean Cyl-1 $^{14}C/^{13}C$ ratio and the mean OXI $^{14}C/^{13}C$ ratio will increase the overall scatter in Cyl-1 $\Delta^{14}C$. Mean $\Delta^{14}C$ values for the Cyl-1 targets in each wheel ranged from 57.9–62.4‰ (Table 1), demonstrating that the relative $^{14}C/^{13}C$ ratios between the Cyl-1 targets and the OXI targets do vary between wheels. An error in the mean OXI $^{14}C/^{13}C$ ratio on a particular wheel will result in a systematic error in the $\Delta^{14}C$ of Cyl-1 targets on that wheel. Uncertainty in the mean OXI $^{14}C/^{13}C$ ratio can be estimated by dividing the pooled standard deviation in OXI, 2.3‰, by the square root of the number of OXI targets on each wheel, 6. The standard error in OXI is 0.9‰, suggesting that errors in the mean OXI $\Delta^{14}C$ account for a large portion of σ_{BW} of Cyl-1. Improvements in the reproducibility of OXI therefore have the potential to improve the overall precision of CO_2 measurements at LLNL.

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 atmospheric CO_2 samples at LLNL.

Our analysis does not rule out other contributions to the wheel-to-wheel uncertainty. Additional uncertainty may arise from daily variability in several components of the AMS, including 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, stripping, 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 $\Delta^{14}C$ on replicate samples, but our quadrature sum indicates they may be as large as 0.8‰ for measurements of Cyl-1.

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, σ_{tot} = 1.7‰. The precision of $\Delta^{14}C$ in Cyl-1 targets analyzed on 1 wheel was limited by internal uncertainty, σ_{int} = 1.2‰, as the within-wheel repeatability (1.3‰) was comparable to the internal uncertainty. However, the scatter in all 36 targets demonstrated that additional uncertainty is introduced when samples are analyzed on several wheels: σ_{BW} = 1.2‰. 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, sug-

gesting 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 $^{14}C/^{13}C$ ratios in the Cyl-1 targets with another CO_2 reference material that undergoes the same sample handling procedures.

As the LLNL AMS system measures only $^{14}C^{4+}$ and $^{13}C^{4+}$ 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 $^{12}C^{-}$ will be implemented in the low-energy section of the AMS in the near future, and implementation of $^{12}C^{4+}$ detection in the high-energy section is possible in the next few years. Measurement of all 3 carbon isotopes will allow correction of fractionation inside the instrument, further improving the detection capabilities at LLNL.

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