Microscale AMS $^{14}$C Measurement at NOSAMS

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Abstract

Techniques for making precise and accurate radiocarbon accelerator mass spectrometry (AMS) measurements on samples containing less than a few hundred micrograms of carbon are being developed at the NOSAMS facility. A detailed examination of all aspects of the sample preparation and data analysis process shows encouraging results. Small quantities of CO$_2$ are reduced to graphite over cobalt catalyst at an optimal temperature of 605°C. Measured $^{14}$C/$^{12}$C ratios of the resulting targets are affected by machine-induced isotopic fractionation, which appears directly related to the decrease in ion current generated by the smaller sample sizes. It is possible to compensate effectively for this fractionation by measuring samples relative to small standards of identical size. Examination of the various potential sources of background $^{14}$C contamination indicates the sample combustion process is the largest contributor, adding ca. 1 µg of carbon with a less-than-modern radiocarbon concentration.

Although sample size problems can potentially be resolved by adding sufficient diluent carbon of known isotopic composition, an analysis of the uncertainties associated with this approach suggests it may not yield results at a useful level of precision. The mass balance equations

\[ m_x F_x = m_s F_s + m_d F_d \]  

and

\[ m_x = m_s + m_d \]

(where \( m \) designates mass, \( F \) the $^{14}$C fractional abundance, and \( x, s, \) and \( d \) are the composite, the sample, and the diluent) can be rewritten as
\[ (3) \quad F_s = r_x F_x - (r_x - 1) F_d \]

where \( r_x = \frac{m_x}{m_s} \) is the dilution factor. Propagation of error then results in the following equation, where \( \sigma \) is the standard deviation and measurement precision \( P = \sigma_m/m \):

\[
(4) \quad \sigma^2_{F_s} = r_x^2 \sigma^2_{F_x} + (1-r_x)^2 \sigma^2_{F_d} + (F_x - F_d)^2 (2P^2) r_x^2 
\]

Term \( a \) dominates the result; the other two terms can be manipulated toward zero by 1) the use of a \(^{14}\text{C}-\)“dead” diluent (\( \sigma_{F_d} \) approaches zero in \( b \)), 2) choosing a diluent of isotopic composition identical to the sample (\( F_x - F_d \) goes to zero in \( c \)), and/or 3) optimizing measurement precision, \( P \), in \( c \). Choosing optimal realistic values of \( P = 0.01 \), \( F_x - F_d = 0.5 \), \( \sigma_F = 0.004 \), \( \sigma_F = 0.005 \) at 500 \( \mu \text{gC} \), and \( \sigma_F = 0.010 \) at 100 \( \mu \text{gC} \), Figure 1A shows the calculated error in the \(^{14}\text{C} \) content of the original sample, \( \sigma_{F_F} \), is inversely related to sample size, rendering dilution least practical in the size range where it would be most useful.

Detailed examination of equation (4) clarifies the potential as well as limitations of dilution. While term \( c \) is always small due to the \( P^2 \) multiple, and term \( b \) can be kept artificially small, it is evident that in a precise formulation of this equation, \( \sigma^2_{F_x} \) in term \( a \) is a function of the size of the composite. This creates a potential situation in which the increased uncertainty due to the dilution factor is partially offset by the better precision obtainable when measuring the larger sample. Figure 1B highlights \( \sigma_{F_x} \) for a representative 10 \( \mu \text{gC} \) sample diluted over a range of \( r_x \), where the size dependence of \( \sigma_{F_x} \) has been approximated as \( \sigma_{F_x} = 0.06e^{0.018r_x} \) and the other variables of equation (4) are given the same values as in Figure 1A. The improved measurement precision at larger sample size makes dilution by a factor of 10 just as precise as 5-fold dilution, but uncertainties ca. 100‰ remain impractical for most applications. Dilution may still be the option of choice, however, for extremely small, irreplaceable samples for which the risks involved with uncertain graphitization and AMS performance are too great.

**Results and Discussion**

Between September 1994 and September 1996 we analyzed a total of five small sample wheels at NOSAMS, one of which was composed almost entirely of standards containing 150 \( \mu \text{gC} \), for the purpose of evaluating AMS performance in the analysis of microgram-sized targets. The rest of the wheels each contained 10-20 specially prepared small HOxI and HOxII standards spanning the range of sample sizes being analyzed, in place of the usual 1 mg standards. We therefore have raw data for a total of 51 small HOxI and 32 small HOxII standards with which to assess AMS performance within this size range.

**Optimization of Graphite Production Reaction**

There are many variables that could potentially control the outcome of the \( \text{CO}_2 -> \text{C(gr)} \) reduction; our goal was to identify and optimize reaction conditions for the most critical of these factors. The percent conversion of \( \text{CO}_2 \) to graphite was used as a direct index of reaction performance. Preliminary examination of the reaction yield data showed that production of high-quality small samples is highly sensitive to minor variations in reaction conditions, but the scatter exhibited in the results and the large number of variables precluded the use of standard regression analysis methods.
Fig. 1. A. Calculated error $\sigma_{Fs}$ for dilution to a conventional sample size of 500 $\mu$gC (a) and for dilution to 100 $\mu$gC only (b). B. Calculated error $\sigma_{Fs}$ for dilution of a 10 $\mu$gC sample up to $r_x=10$ using a variable $\sigma_{Fx}=0.06e^{0.01Mx}$. Increased precision in $\sigma_{Fx}$ partially offsets the dilution error.
TABLE 1: Factorial Analysis Parameters

<table>
<thead>
<tr>
<th>Variable</th>
<th>Median</th>
<th>(-)</th>
<th>(+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (T)</td>
<td>608°C</td>
<td>606</td>
<td>610°C</td>
</tr>
<tr>
<td>Carbon:Cobalt (R)</td>
<td>59.2 µgC/mg Co</td>
<td>58.8</td>
<td>59.6</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_2$ (H)</td>
<td>3.20 (mol:mol)</td>
<td>3.16</td>
<td>3.24</td>
</tr>
<tr>
<td>Quantity (Q)</td>
<td>40 µg C</td>
<td>39.6</td>
<td>40.4</td>
</tr>
</tbody>
</table>

Fig. 2. A. $2^3$ factorial analysis of T, R, and H effects on reaction yield. B. $2^4$ factorial analysis of T, R, H, and Q effects on reaction yield. A (+) indicates the upper range of the factor improves % yield, while a (-) indicates the lower range improves % yield. The variables are described in the text.
Verkouteren and Klouda (1992) have previously demonstrated the utility of bi-level factorial
design analysis in unraveling the complexities associated with graphite preparation. A
preliminary inspection of our data suggested which variables were likely to be the most
significant controls on the graphite reaction. A two-level, $2^3$ factorial design was applied to
determine the relative dependence of reaction yield on temperature (T), carbon:cobalt ratio (R),
and $H_2$CO$_2$ ratio (H). The assumption had been made that a fourth variable, the sample
quantity (Q), has a positive correlation with reaction success - large samples are easier to reduce.
To test this assumption, the effect of size on reaction yield was added, creating a $2^4$ factorial.

The $2^3$ matrix [$T \times R \times H$] and the $2^4$ matrix [$T \times R \times Q \times H$] were calculated using a table of
contrast coefficients (equivalent to Yates' algorithm) (Box, Hunter, and Hunter 1978). Data
from our first batches of small HOxI and HOxII standards were divided into two levels, (-) and
(+), around the median of the range of each variable (Table 1); data whose analytical error
crossed the median were eliminated. The 46 acceptable samples were distributed fairly
uniformly among the 8 categories of the $2^3$ matrix (min $n_i$=3). The result of the $2^4$ matrix is less
robust due to a lack of replicate data points for many of the 16 run categories. In both cases
error bars are calculated from a pooled estimate of run variance. Results of the factorial
analyses (Fig. 2) confirmed qualitative trends that had been observed in the data: reaction yield
improves at lower temperatures and larger samples favor better yields. Cobalt-catalyzed
reduction appears to be more successful at temperatures below 608°C, lower than the 625°C
normally employed when using dendritic Fe. Since this discovery, we have adopted 605°C as
our reaction temperature when preparing small samples on cobalt. Yields are routinely > 90%
under these conditions. We have no direct evidence of the mechanistic effect the low
temperature has on the system, but one possibility includes partial inactivation of the catalyst
surface at higher temperatures. Variation in H is not significant over the small range of values
studied, and the slight negative dependence on R is probably unimportant as well.

AMS Performance of Small Samples

Since we are interested in determining AMS performance under conditions of reduced carbon
ion beam intensity, all the isotope ratio data reported here have been compared to measured $^{12}$C
ion current ($I_{^{12}}$) rather than sample size. The $I_{^{12}}$ beam is measured in a Faraday cup after the
110° spectrometer magnet, after being chopped by a factor of ca. 95. The currents shown are
electrical currents of the $^{12}$C$^{3+}$ ions; particle currents would be 1/3 of these values. Figure 3
shows that $I_{^{12}}$ is a reasonable proxy for sample size, and we believe that the precision of the
measured isotope ratios is likely to be related more directly to $I_{^{12}}$ than to the overall sample size.
Both $I_{^{12}}$ and measured isotope ratios are also found to be time-variant within the accelerator as
discussed below, a further indication that bulk sample size is not as informative a performance
index as is the measured $I_{^{12}}$.

Figure 4 shows the dependence on current of the $^{14}$C/$^{12}$C ratios obtained for small standards.
Individual time-point measurements obtained for each target are compared to the average
isotope ratios of HOxI and HOxII standards of regular (1 mg) size that were included in the
small-sample wheels. These data represent an average of 4 min per point (roughly $10^3$ counts),
with 3-6 points recorded per standard. Three samples that failed to generate any stable,
measurable current have been excluded. These contained < 10 $\mu$gC, and are defined as “AMS
failures”. Both HOxI and HOxII small standards show a characteristic decrease in $^{14}$C/$^{12}$C
below 100 $\mu$gC; a relationship that has been observed previously by Klinedinst et al. (1994),
Brown and Southon (1997), and other groups.
Fig. 3. Observations showing that the $^{12}$C current measured for small samples varies with size, according to the approximate relationship $I_{^{12}C} = 0.9M$. $M$ = mass of carbon in micrograms; $I_{^{12}C}$ = $^{12}$C current in nanoamperes.

Concurrent AMS measurement of the $^{13}$C/$^{12}$C ratio for small standards also shows apparent fractionation at lower sample currents, although the relationship is somewhat less pronounced for $^{13}$C than for $^{14}$C. It is possible that instrument tuning affects $^{13}$C detection differently than it affects $^{14}$C, and therefore generates a slightly less uniform relationship between $^{12}$C and $I_{^{12}C}$. Figure 5A shows the difference between the AMS measured $\delta^{13}$C for small HOxI and HOxII standards and the pre-graphite $\delta^{13}$C values of the CO$_2$ from which they were prepared (measured on a VG Prism stable isotope mass spectrometer). The difference is expressed as $\Delta\delta^{13}$C = $\delta^{13}$C$_{AMS} - \delta^{13}$C$_{VG}$. The VG Prism $\delta^{13}$C values for HOxI are -19.0 to -19.3‰ and for HOxII are -17.6 to -17.7‰.

Fig. 4. Dependence of the measured $^{14}$C/$^{12}$C isotope ratios for HOxI (A) and HOxII (B) small
samples on the generated $^{12}\text{C}$ ion current. Ratios have been normalized to average values obtained for HOxI and HOxII standards of conventional size.

Fig. 5. A. $^{13}\text{C}$ fractionation of HOxI and HOxII small samples as a function of the generated $^{12}\text{C}$ ion current for all discrete time points. B. $\Delta \delta^{13}\text{C}$ and $I_{12}$ variation within samples as a function of elapsed measurement time.

There are several potential reasons for the observed isotope ratio dependence on sample size. Explanations that invoke fractionation or contamination during the graphite production step are among the more popular candidates. Van der Borg et al. (1997) showed that fractionation can occur during the graphitization process: reactions that failed to reach completion produced graphite that was depleted in $^{14}\text{C}$ and $^{13}\text{C}$, and left residual CO$_2$ that was isotopically enriched. However, examination of our yield data indicates there is no apparent correlation between percent conversion of CO$_2$ to graphite and the isotope ratios subsequently measured during
AMS analysis. This argues against a fractionation effect induced during any phase of the sample preparation. Similar results have also been obtained by McNichol et al. (1992).

Another possible explanation for the decrease in isotope ratios is the addition of a background carbon contaminant during graphite production or during analysis of the AMS targets. Data published by Brown and Southon (1997) for a very similarly behaving suite of small standards indicate that our source of contamination, if any, may be independent of sample size. They suggest carbon contained within the catalyst matrix or residual carbon in the AMS ion source. At NOSAMS, 14C-“dead” graphite measured immediately following modern samples fails to show significant sample cross-talk or other problems inherent to the source. We believe it is also unlikely that the isotope ratios are being altered by the presence of large amounts of background carbon within the Co catalyst. This is based on observation of instances when isotope ratios and 12C currents co-vary within individual samples (Fig. 5B). If background carbon were incorporated within the sample during processing or were contained in the Co matrix, a time-series plot would be expected to show a constant or randomly varying isotope ratio over the course of analysis, not the systematic decrease in isotope ratio we have observed for these and many additional samples. The Δδ13C and I12 changes in Figure 5B appear to be a function of elapsed measurement time. These data suggest that the effective fractionation we have observed is primarily a function of machine conditions, not the result of isotopically light carbon incorporated uniformly within the sample during preparation.

Support for this hypothesis comes from consideration of the differing beam dynamics at high and low current levels. Instrument tuning is always carried out using 1-mg standards. The current beams generated by these large targets have a correspondingly higher beam divergence than do beams generated by small samples, due to increased Coulomb repulsion in the presence of higher space charge density. The instrument is tuned to compensate for the fractionation induced within the large sample. Because Coulomb repulsion affects lighter isotopes more strongly, it is possible that 13C detection is less efficient relative to 14C detection for large samples, but that the detection difference may be less pronounced for low-density small samples. The net effect would be an apparently lower 14C/12C ratio for small samples. While this argument is qualitative, it provides a physically plausible mechanism for the observed effects. Details of the beam dynamics model can be found in von Reden et al. (1998).

At NOSAMS, we have found different explanations for the sources of background contamination and fractionation than have previously been identified by some of the AMS groups mentioned in the above discussion. This points to the need for individual AMS facilities to conduct independent and thorough evaluations of their analytical procedure, because it is likely that the results will display characteristics unique to each facility.

Conclusions

At NOSAMS, preparation and AMS analysis of samples containing 10-150 μgC has exhibited an encouraging level of success. These results have promising implications for several oceanographic and environmental research areas, including the pore water carbon cycle, oceanic dissolved organic carbon studies, and molecular-level 14C analysis. All are areas in which available sample size has been the main limitation on the use of 14C AMS.

1. Small quantities of CO2 can be converted reliably into high-quality graphite for AMS. Reduction is carried out over cobalt catalyst at 605°C in small-volume reactors. The reaction appears especially sensitive to temperature, showing a decrease in reaction yield at high temperature.

2. AMS targets containing 150 μgC are prone to machine-induced isotopic fractionation, which appears directly related to the lower levels of carbon ion
current generated by these samples. This may be caused by inherent limitations in
the instrument design and tuning capabilities of the NOSAMS accelerator.

3. Carbon contamination within the NOSAMS source does not appear to be significant
enough to affect the outcome of small target analyses; neither does addition of
modern-equivalent carbon during the graphitization process. Time-variant data for
HOxl and HOxII targets is evidence against the addition of a large amount of
“dead” carbon during graphitization, although amounts equivalent to less than the
machine fractionation effect may be present. Carbon added during the combustion
of small organic samples is still under investigation, but preliminary work indicates
this blank is ca. 1 µg and has significantly less than modern 14C concentration.

4. It is possible to compensate effectively for machine fractionation and blank carbon
contributions by measuring small samples relative to size-matched small standards.
There are two possible options for preparation of the small standards: reduction of
small splits of a large, homogeneous gas standard, or combustion and subsequent
reduction of individual small aliquots of the original standards. When analyzing
small, combusted organic samples relative to small HOxl and HOxII standards,
choosing the first option requires a subsequent blank correction to the sample f m,
while the second option would eliminate this correction. Because it is more difficult
and less time-efficient to prepare individually combusted standards of precise mass,
we continue to perform our routine analyses with small splits of a large standard
and then apply a separate combustion blank correction. Small HOxl and HOxII
standards measured relative to each other using this approach no longer show a
size-dependent isotopic fractionation.