THE RAPID PREPARATION OF SEAWATER $\Sigma CO_2$ FOR RADIOCARBON ANALYSIS AT THE NATIONAL OCEAN SCIENCES AMS FACILITY


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ABSTRACT. We have established a laboratory for extracting $\Sigma CO_2$ from seawater samples for AMS analysis of the radiocarbon content. The seawater samples are collected at sea, poisoned and stored until analysis in the laboratory. Each sample is acidified; the inorganic carbon is stripped out as $CO_2$ with an inert carrier gas and then converted to graphite. We present results for Buzzards Bay surface $H_2O$ and $Na_2CO_3$ standards that demonstrate we strip >98% of inorganic carbon from seawater. Stable isotope analyses are performed to better than 0.2‰, and the reproducibility of $^{14}C$ measurements on Buzzards Bay seawater is better than 13‰. Finally, we compare data from samples collected in 1991 to those collected in the 1970s and to large volume samples.

INTRODUCTION

Early studies demonstrating the viability of using accelerator mass spectrometry (AMS) to measure $^{14}C$ in seawater inorganic carbon (Bard et al. 1988; Kromer et al. 1987; Ostlund et al. 1987a; Schlosser et al. 1987) led to the inclusion of an AMS $^{14}C$ sampling program in the World Ocean Circulation Experiment (WOCE). One component of the WOCE Hydrographic Program (WHP), the collection of thousands of seawater samples for AMS $^{14}C$ analysis, was a driving force for the establishment of the National Ocean Sciences AMS (NOSAMS) facility at the Woods Hole Oceanographic Institution (WHOI). The WOCE program requires a precision of 5–10‰ for the AMS analysis of $\Delta^{14}C$ (Joyce, Corry and Stalcup 1991) in surface seawater samples and a precision of 3–4‰ for deepwater samples, i.e., samples below ca. 1000 m.

Östlund et al. (1987a), Bard et al. (1987) and Kromer et al. (1987) made the first AMS measurements of seawater. In general, the methods used to strip $CO_2$ from an acidified seawater sample were either bubbling with a carrier gas (Bard et al. 1987; Ostlund et al. 1987a) or extraction with a vacuum source (Dörr and Münnich 1980). Bard et al. (1987) reported results with a standard deviation of 11‰, Kromer et al. (1987) reported a standard error of 5‰ and Ostlund et al. (1987a) reported a precision of 5–10‰.

Our laboratory was set up for the rapid preparation of inorganic carbon in seawater for analysis by AMS. In this paper, we describe in detail our method for extracting $CO_2$ from seawater, and we demonstrate our ability to accurately and reproducibly prepare seawater samples for AMS. We also present results from the analysis of local surface seawater and two WOCE $^{14}C$ AMS depth profiles.

METHODS

Seawater for all WOCE analyses is collected in pre-weighed 500-ml borosilicate glass bottles with high-quality ground-glass stoppers and poisoned according to a published protocol (McNichol and
Jones 1991). Dissolved inorganic carbon (ΣCO₂) is extracted as CO₂ gas from the samples on the vacuum line shown in Figure 1; the vacuum system consists of a molecular drag pump in tandem with a diaphragm pump. The samples are stripped in the bottles in which they are collected. Up to five samples can be attached to the line at one time. Samples to be analyzed are weighed and transferred to a glove bag where stripping probes are attached in an N₂ atmosphere (insert, Fig. 1). The bottles are then attached to Region I of the vacuum line, and the line is evacuated up to the valves on the stripping probe (Valves V1 and V2). Each sample is acidified by adding 4 ml of 85% H₃PO₄ by injection through a rubber septum. When the line has been evacuated, high-purity N₂ gas (99.99%) is added to Regions I, II and III to a pressure of ca. 0.8 atm. A cold bath at −80°C is placed on the trap in Region II and liquid nitrogen baths (−190°C) are placed on the loop traps in Region III. When the cold traps are in place and all the valves in the circulation loop are open, a recirculating pump (Parker Hannifan Metal Bellows MB-10) is turned on, forcing the carrier gas through the fritted end of the probe and producing a stream of fine bubbles throughout the seawater. Gaseous CO₂ partitions into the N₂ bubbles and is swept into the cold traps where it is frozen down. After 10 min, the pump is shut off, the N₂ carrier gas is slowly pumped away, the liquid nitrogen baths on the loop traps are replaced with −80°C cold baths and the CO₂ is collected in a calibrated volume (Region IV). The gas pressure is recorded and used to calculate the concentration of CO₂ (ΣCO₂) in each sample; the gas sample is then transferred to a storage manifold (Region V). Typical yields for seawater samples are ca.1 mmol of CO₂. While the sample is being quantified, the vacuum line is prepared for the next sample. The average analysis time is ca. 45 min.

After ten samples have been stripped, the storage manifolds are removed from the water line and attached to the graphite transfer line (Fig. 2) where the gas is split into aliquots for graphite target

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Fig. 1. Water stripping line and stripping probe (insert). Ball and socket O-ring joints (B/S) were added to facilitate dismantling and cleaning. The use of a glass system reduces the number of parts that must be replaced due to corrosion from salt water vapor. The stripping probe is designed to fit directly on bottles with a standard taper high-quality ground-glass joint. Valves V1 and V2 are integral parts of the stripping probe and are not part of the stripping line.
Preparing Seawater $\Sigma$CO$_2$ for AMS Analysis

Fig. 2. Schematic diagram of graphite transfer line for seawater samples. A blowup of the reactor is shown in the insert. Sample manifolds are attached, and each sample is sequentially transferred to the cold finger. From the cold finger, splits of each sample are transferred to an isotope ratio mass spectrometer, to an archive tube and to a graphite reactor.

preparation (20%), stable isotope ratio analysis (10%) and archiving (70%). The graphite target preparation method used at NOSAMS has been described elsewhere (McNichol et al. 1992). Briefly, CO$_2$ is transferred to a reactor, where it is catalytically reduced to carbon filaments at high temperature (625°C) using H$_2$ gas as the reducing agent and Fe as the reduced metal catalyst; the reaction takes ca. 4 h. During 1992 and the first half of 1993, stable isotope analyses were performed on three different mass spectrometers—a VG Micromass 602E in the laboratory of Lloyd Keigwin (WHOI), a VG Prism in the Earth and Planetary Sciences Department at Harvard University and a VG Prism at our facility. Since June 1993, most stable isotope analyses for seawater samples are performed in the NOSAMS sample preparation lab on an in-line VG Optima mass spectrometer.

We use two types of samples as standards—Na$_2$CO$_3$ solutions and local surface seawater. We prepare our Na$_2$CO$_3$ standards in batches of 9–12 samples; Na$_2$CO$_3$ is dried overnight in a 250°C oven; ca. 424 mg are weighed accurately (± 0.01 mg) and quickly transferred to a 2-liter volumetric flask. Exposure to air is minimized because Na$_2$CO$_3$ absorbs water from air and forms a basic solution that absorbs CO$_2$ from the surrounding air. This is more likely to have an effect on the isotopic measurements than on the concentration measurements. Distilled water is degassed by bubbling with N$_2$ for at least 1 h, added to the volumetric flask and the solution is transferred to 500-ml sample bottles in an N$_2$-filled glove bag. We have found that degassing reduces the inorganic carbon concentration of distilled H$_2$O by ca. 85% to a level where it contributes only 0.3% of the carbon in our standards. Local surface seawater (0–1 m depth) from Buzzards Bay, Massachusetts is collected in 20-liter carboys and transported to the sample preparation laboratory, where it is transferred to 500-ml sample flasks, poisoned with 100 $\mu$l saturated HgCl$_2$ solution, capped and stored until processing. After
preparation, both the Na₂CO₃ and Buzzards Bay seawater standards are handled in exactly the same manner as the samples. Our standard procedure is to measure 1 Na₂CO₃ and 1 Buzzards Bay seawater standard after each suite of 16 WOCE samples.

RESULTS

From January 1992 to July 1993, we stripped over 850 samples and standards. Figure 3 shows concentration and stable isotope results for the Na₂CO₃ and Buzzards Bay samples. The Na₂CO₃ graph comprises data from many different batches and the Buzzards Bay graph displays results from four sample collections. To determine our analysis precision, we averaged the results from each data set shown in Figure 3, and rejected any point that deviated from the average by >3 standard deviations. Using the selected data, we calculate that for the Na₂CO₃ standards, we extracted 100.9 ± 2.2% of the inorganic carbon added to the standards and measured an average δ¹³C of −1.46 ± 0.18‰ (Table 1). To study the Buzzards Bay data, we separated the samples into batches to remove seasonal and interannual variability. From the two batches for which we have enough data (2/92 and 8/92), we measured the concentration to at least ± 0.04 mmol kg⁻¹ and δ¹³C to better than ± 0.15‰ (Table 1). The precision observed in the August 1992 samples is greatly improved from that observed in the February 1992 samples. We believe this is due to the steady improvement of our procedures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΣCO₂ (mmol kg⁻¹)</th>
<th>n</th>
<th>δ¹³C (%)</th>
<th>n</th>
<th>Δ¹⁴C ‰</th>
<th>n</th>
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<tbody>
<tr>
<td>Buzzards Bay</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2/91</td>
<td>1.953 (0.044)</td>
<td>3</td>
<td>1.125 (0.211)</td>
<td>2</td>
<td>61.5</td>
<td>1</td>
</tr>
<tr>
<td>2/92</td>
<td>1.981 (0.034)</td>
<td>36</td>
<td>1.183 (0.146)</td>
<td>31</td>
<td>65.4 (12.8)</td>
<td>13</td>
</tr>
<tr>
<td>8/92</td>
<td>1.896 (0.040)</td>
<td>16</td>
<td>1.244 (0.062)</td>
<td>14</td>
<td>69.4 (12.1)</td>
<td>4</td>
</tr>
<tr>
<td>6/93</td>
<td>1.782 (0.159)</td>
<td>3</td>
<td>1.318 (0.030)</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%Yield</td>
<td>100.91 (2.20)</td>
<td>61</td>
<td>−1.457 (0.180)</td>
<td>52</td>
<td></td>
<td></td>
</tr>
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</table>

Some of the Buzzards Bay samples were used in a sample storage experiment; bottles collected in February 1991 were stripped and analyzed over a 500-day period (Fig. 4). Within the error of the analyses, it is not possible to distinguish the sample analyzed almost 1.5 yr after the date of collection from those analyzed immediately after collection.

We have analyzed Buzzards Bay samples collected in February 1991, February 1992 and August 1992 for Δ¹⁴C (Table 1, Fig. 4). Samples collected in February 1992 were analyzed 13 times using AMS between March 1992 and March 1993. For this period, we calculate a weighted average Δ¹⁴C of 65.4‰ with a standard deviation of 12.8‰. Reported Δ¹⁴C values have been corrected for ¹³C fractionation and adjusted to 1950 according to Stuiver and Polach (1977). At present, we observe no significant seasonal or annual differences. Although this particular set of samples does not reflect it, in recent months, our method has produced results demonstrating a precision of ± 3‰ for individual AMS analyses (Jones et al. 1994).
Fig. 3. Concentration and stable isotope results from (A) Na₂CO₃ and (B) Buzzards Bay standards. Sample number refers to the order in which the standards were stripped; all were stripped between January 1, 1992 and June 31, 1993. The dates in the key (B) refer to the month and year in which the batch of seawater was collected.
We have analyzed > 800 WOCE seawater samples and present $^{14}$C data from two stations. The samples were collected during Cruise CGC-91 along WOCE line P16N. We present data from Stations 12 (35°N, 152°W) and 48 (42°N, 152°W) (site locations are shown in Fig. 5). In Figure 6, the WOCE data are compared to those from nearby GEOSECS stations and from samples measured using the β-decay counting technique. The WOCE samples were collected in March 1991, stripped and converted to graphite between January 1992 and July 1992, and analyzed on the AMS between September 1992 and December 1992.

**DISCUSSION**

To produce useful data for the WHP, we must provide results with an overall precision of ±5–10‰ in surface seawater and ±3–4‰ in deepwaters. These requirements are driven by the magnitude of the $^{14}$C gradients observed in the different layers of the ocean. We have demonstrated through the analysis of standards that we can reproducibly and accurately strip CO$_2$ from seawater for stable and $^{14}$C isotopic analysis. To achieve a precision of ±3‰ in our $^{14}$C measurements, we must know the δ$^{13}$C of the sample to better than 1‰, so that the stable isotope fractionation correction does not
Fig. 5. Sample collection sites in North Pacific Ocean. Stations 12 and 48 were occupied in 1991 as part of the WHP, and Stations 201 and 202 were occupied in 1973 as part of the GEOSECS Program.

introduce a significant error to our final number. We have shown that we know the δ13C of the CO2 gas stripped from seawater to much better than this (± 0.06–0.18‰), and we make the assumption that reducing CO2 to graphite does not greatly increase this error. Fractionation that is constant for all samples and standards will not compromise the overall precision as long as the standard deviation is < 1‰. We reported previously that our graphitization process introduced a stable isotopic fractionation of ca. 1.2 ± 0.3‰ that was constant for a wide range of δ13C values (McNichol et al. 1992). More recent results show that, because of improvements in our techniques, no fractionation is introduced during the graphitization process (Osborne et al. 1994).

We measure the inorganic carbon concentration as an internal laboratory quality check. Our average measured concentration for Buzzards Bay seawater in February 1991 (1.95 ± 0.04 mmol kg⁻¹) agrees with the measurement on three samples from the same batch using a coulometric method (Goyet and Hacker 1992) as an independent measure (1.938 ± 0.008 mmol kg⁻¹). We do not attempt to make a precise measurement of this parameter, and we report an error of ± 2%. One potential source of error in our concentration measurement is the lack of precise temperature control during our manometric measurements. For example, if the temperature of the glass expansion volume is just 3°C hotter or colder than the air surrounding the thermometer we use to read the ambient tem-
perature, we will introduce an error of ~1%. Other potential sources of error we have identified are listed in Table 2. Most of these sources affect only the concentration measurement and not the isotopic ratios.

<table>
<thead>
<tr>
<th>Table 2. Potential Sources of Error in Seawater Measurements</th>
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<tr>
<td>Error</td>
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<tr>
<td>Exclusion of weight of stopcock grease in “empty” bottle weight</td>
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<tr>
<td>Chipping of glass bottles during sampling/processing</td>
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<tr>
<td>Small temperature fluctuation during manometric measurements</td>
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<tr>
<td>Multiple gas transfers</td>
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Fig. 6. A. NOSAMS data from Stations 12 (▲) collected in 1991, GEOSECS data from Stations 201 (○) and Station 202 (□) collected in 1973 (Östlund et al. 1987); B. comparison of NOSAMS small volume AMS results (▲) with RSMAS Tritium Laboratory large volume counting results (△) (Östlund 1992) from Station 48 collected in 1991.
The results of the storage experiment indicate that samples can be stored for prolonged periods without jeopardizing their integrity. This is important for the analysis of WOCE samples, because investigators in the WOCE program are collecting seawater samples at a much faster rate than they can be analyzed, and samples remain in their collection boxes for prolonged periods. Although we strip the samples as quickly as possible, often well before they are analyzed on the AMS, some samples can be stored for as long as 2–2.5 yr before analysis. Therefore, it was essential for us to demonstrate that samples can be stored for long periods of time without undergoing significant changes in concentration and/or isotopic composition.

The comparison of our data to those collected from similar locations during the GEOSECS program in 1973 (Östlund et al. 1987b) and to those collected in large-volume Gerard barrels provides further confirmation of the validity of our results (Fig. 6). At Station 12 (Fig. 6A), we observe that, below 1000 m within the error of the measurements, our analyses agree with the GEOSECS data, but that above this depth, the results differ. In the surface waters, results from the water samples between 0- and 200-m depth reflect the decrease in atmospheric 14C concentration from 1973 to 1991 and, between 200 and 800 m, the results reflect the penetration of the “bomb signal” deeper into the water column. Below 1000 m, we do not expect the seawater Δ14C to have changed significantly over the 20-yr period. At Station 48 (Fig. 6B), our data are compared to those reported by Östlund (1992) from 250-liter samples. We observe excellent agreement; the average reported error for the large-volume samples is ±2‰ and, for the AMS samples, ±3–7‰. This comparison shows that results from the two methods are indistinguishable and that AMS will provide a viable substitute for large-volume oceanographic sampling.

CONCLUSION

We have successfully established a laboratory capable of rapidly analyzing large numbers of seawater samples for AMS 14C analysis. We have analyzed >800 seawater samples since 1992 with a precision and accuracy that meet the demands of the WHP, and anticipate analyzing at least 2000 samples per year in the future. With the anticipated completion of our laboratory automation this year, increased throughput will not present a problem, and we should easily meet the demands of the U.S. WOCE 14C program over the next five years.

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REFERENCES


Goyet, D. and Hacker, S. D. 1992 Procedure for calibra-


