ESTABLISHING WATER SAMPLE PROTOCOLS FOR RADIOCARBON ANALYSIS AT LAC-UFF, BRAZIL

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ABSTRACT. Since the establishment of the first radiocarbon accelerator mass spectrometry facility in Latin America in 2009, the Radiocarbon Laboratory team of Universidade Federal Fluminense (LAC-UFF) has worked to improve sample preparation protocols and increase the range of environmental matrices to be analyzed. We now present the preliminary results for DIC sample preparation protocols. The first validation tests include background evaluation with pMC value (0.35 ± 0.04) using bicarbonate dissolved in water. We also analyzed surface seawater resulting in pMC value (101.38 ± 0.38) and a groundwater previously dated from LEMA AMS-Laboratory with pMC value (12.30 ± 0.15).

KEYWORDS: protocols, radiocarbon, water samples.

INTRODUCTION

In Brazil, the demand for radiocarbon (^{14}C) measurements of water samples, both scientifically and economically, comprises ocean, surface freshwater and groundwater. One fifth of the world's freshwater reserve is within Brazilian lands with ca. 111 trillion cubic meters of groundwater. The linear extension of the Brazilian coast has over 8000 km, with 3.6 million km^2 of oceanic waters and very distinctive oceanographic conditions. ^{14}C has been used to determine sources, groundwater recharge, ages and pathways and its measurement in dissolved inorganic carbon (DIC) performed directly in a Brazilian laboratory can simplify sample submission, decrease the costs of analysis, and contribute to increasing the number of scientific studies performed in Brazil in this area.

^{14}C may be used as a tracer of several natural processes (Hanshaw et al. 1965), including pollution and quality changes caused by human activities. There is a special interest in the use of ^{14}C for the chronology of geological formations and determination of groundwater residence times (Cartwright et al. 2020).

The ^{14}C analysis of carbonate species in groundwater can provide information about the recharging of underground deposits as well as its direction and flow (Hanshaw et al. 1965). Concerning seawater, it is important because it is known that the oceans play an important role in the carbon cycle on seasonal to millennial timescales. The ocean circulation redistributes DIC, and the ^{14}C in water is related to the amount of time it has been isolated from exchange with the atmosphere (McNichol and Aluwihare 2007). ^{14}C has horizontal

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Figure 1   An inert headspace performed in a 120-mL bottle, using 50–60 mL of seawater to CO_2 extraction.

and vertical gradients at depth due to decay and slow mixture of deep waters, so that it is a useful tool as a tracer of ocean currents, allowing scientists to determine the sources and ages of deep water bodies besides evaluating the accuracy of ocean circulation models.

Over the years, many methodologies for water sample preparation for ^{14}C analysis have been suggested. Bard et al. (1989) for example, extracted CO_2 from seawater samples in a special vacuum system filled with pure helium and cooled traps. Molnár et al. (2013) showed a system with a double needle with a controlled flow of He as a carrier gas where vacuum was not required. Gao et al. (2014) have developed a method for water sample preparation based on a septum-sealed screw cap vial.

The goal of this study is to evaluate any contamination during the proposed preparation, purification and graphitization processes of water samples. For this purpose, a travertine provided by International Atomic Energy Agency (IAEA), two background samples (Sodium bicarbonate and optical calcite (CA), a surface seawater collected and a groundwater previously date provided by LEMA AMS-Laboratory were prepared and analyzed. The amounts of each reactant used during the process were calculated in order to yield at least 1 mg of carbon at the end of graphitization process.

SAMPLE PREPARATION

A headspace is the space filled with an inert gas (Figure 1) in a liquid/gas system. Glass bottles filled with solution were sealed with a special rubber cap (which allows being drilled by a needle) in order to avoid air contact and contamination (Molnár et al. 2013; Gao et al. 2014) then they were disposed upside down, two needles were attached into the cap and nitrogen was pulled through one of the needles using the other one as a drain, therefore, water is replaced by N_2 gas, to form a headspace.
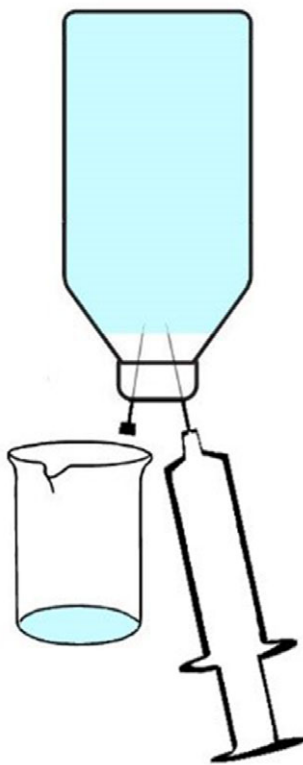
Figure 2 The scheme of creation
of an inert headspace.

The volume of gas displaces the same volume of water which is extracted (Figure 2). The headspace of the first samples analyzed in the LAC-UFF were performed as described above. For the samples described in Table 2, a glove bag was used to make the headspace.

A quantity of 250 mL of ultrapure water was treated with 6 g of NaCl and acidified to pH 5 by addition of 4 mL of HCl 0,1M in order to favor carbonate dissolution since pH and temperature influence $CaCO_3$ solubility (Coto et al. 2012). Approximately 22 mg of IAEA-C2 and CA were dissolved in samples of 120 mL of the solution previously prepared. An inert headspace (Figures 1 and 2) was made for each of them; the bottles were attached to the vacuum line in order to create a vacuum condition in the headspace, to ease the release of CO_2 dissolved in liquid phase. The process was followed by the introduction of 1 mL of 85% phosphoric acid into the bottles, which were kept during 4 days at 25°C, and at 40°C during one night. The gas was purified in a stainless steel vacuum line using dry ice/ethanol and liquid nitrogen traps and graphitization was performed by the zinc reduction method following (Xu et al. 2007) at 550°C (Macario et al. 2015).

At first, solid sodium bicarbonate (S0) was prepared as background samples in order to test the bicarbonate system. In a glass vial 1 mL of 85% phosphoric acid was reacted with 7 mg of solid sodium bicarbonate. After that 4 background samples (S1, S2, S3, and S4) were prepared by

Table 1   Results for sodium bicarbonate in solid state and dissolved in water controlling the extraction of time. These graphites were analyzed at CAIS.

#IDLAC-UFF	Sample	Extraction time (min)	CO_2 pressure (psia)	CO_2 (µmol)	pMC
170073	S0	10	2.06	60	1.33 ± 0.02
170180	S1	10	0.656	17	0.95 ± 0.047
170181	S2	15	0.930	31	0.35 ± 0.041
170179	S3	20	1.556	48	0.37 ± 0.04
170062	S4	35	5.275	156	4.43 ± 0.101
—	S5	50	1.776	57	—

dissolving 700 mg of sodium bicarbonate ($NaHCO_3$) in a volume of 1 L of ultrapure water, and a volume of 120 mL was taken and placed in the glass bottles. The bottles were sealed, an inert headspace was made and 1 mL of 85% phosphoric acid was introduced into each of the bottles, which were kept under heating (40°C) during four days.

Under different conditions, a bicarbonate solution (S5) with 70 mg of bicarbonate diluted in 120 mL of ultrapure water was prepared. An inert headspace was made, followed by the addition of 1 mL of 85% phosphoric acid. The system was kept at 25°C for 5 days, in order to evaluate the influence of temperature on bicarbonate reactivity.

In this work, one previously cleaned bottle of 120 mL of seawater (W1) was collected. This sample was collected on sea surface in Niterói, Rio de Janeiro in January 2018. An inert headspace was made, the system was evacuated, and the same process was followed by the introduction of 1 mL of 85% phosphoric acid into the bottles. The sample was kept for 4 days at 25°C, and at 40°C overnight.

After the hydrolysis in all samples, the CO_2 generated in the reaction was purified in the vacuum line and graphitized (Macario et al. 2015). All samples were prepared and the graphitization were performed at LAC-UFF. The cathodes with graphite were analyzed by AMS in collaboration with the Center for Applied Isotope Studies at the University of Georgia – CAIS (Cherkinsky et al. 2010), Australian National University (ANU) (Fallon et al. 2010) and at LACUFF in a Single Stage Accelerator Mass Spectrometry SSAMS system built by NEC (Linares et al. 2015).

RESULTS AND DISCUSSION

The amounts of gas produced in the purification process, their respective extraction times, and percent of modern carbon (pMC) obtained for $NaHCO_3$ samples, are shown in Table 1. These samples were prepared at LAC-UFF and the graphite produced was measured at CAIS.

It was observed that the longer the extraction, the larger the amount of gas obtained, and the amount of graphite was correspondingly larger, but a longer time of extraction favors contamination. The background sample results show that the experimental apparatus was efficient, when the contamination by modern carbon was less than the standardized value of 0.4 pMC for background samples (Varsányi et al. 2011).

Table 2 Results for reference materials (CA and IAEA-C2) dissolved in MiliQ water and varying some parameters in the sample preparation and the time extraction in the graphitization line. These graphites were analyzed at ANU.

#IDLAC-UFF	Composition	Sample (mg)	HCl 1M (mL)	H_2O (mL)	Time of extraction	Pressure of CO_2 (psia)	CO_2 (μmol)	pMC	OBS
180325	CA	71.4	1.0	50	1:25h	1.800	57	1.25 ± 0.26	Bubbles and a little cloudy
180326	CA	45.3	0.5	20	1:25h	0.955	30	2.11 ± 0.26	
180327	CA	70.1	1.0	50	1:00h	1.469	55	0.78 ± 0.26	Undissolved residue
180328	CA	72.4	1.0	50	0:30h	1.020	31	1.10 ± 0.26	Undissolved residue
180329	CA	24.4	2.5	50	1:10h	0.573	16	84.32 ± 0.36	Bubble in the tube
190132	C2	150	2.5	50	0:30h	1.553	46	42.43 ± 0.17	Presence of undissolved solids
190133	C2	148	2.5	50	1:00h	1.724	52	42.70 ± 0.18	Presence of undissolved solids
190134	C2	149	2.5	50	1:30h	1.971	58	42.52 ± 0.15	Presence of undissolved solids

It was also observed for seawater that even for a shorter extraction time, the yield of gas was larger when the system was subjected to a temperature increase, because it favors CO_2 release from liquid to gas phase. The same effect was observed in background sample (S5) in relation to the others (S1, S2, S3, and S4) submitted to temperature increase. Unfortunately, the graphite of sample (S5) was not measured at the AMS.

The extraction time is an important parameter to avoid contamination during the CO_2 purification step. In this first study, we aimed to control the extraction time. As shown in Table 1, the best result was for sample S2, which was prepared and heated at 40°C during 4 days, using an extraction time of 15 min approximately. A pMC value of 0.35 ± 0.04 was obtained that is in agreement with background values for the sodium bicarbonate sample.

Reference materials diluted in water were submitted to the same procedure described above. Table 2 summarizes the results obtained. These samples were prepared at LAC-UFF and the ^{14}C analyses were performed at ANU.

In order to understand how standard samples would behave with this treatment, we prepared some samples of CA and IAEA-C2. An excess amount of HCl was added to help the dissolution in ultrapure water, making some modifications of the treatment of each sample that are shown in the Table 2.

From the results shown in Table 2, we can infer that an excess of HCl can help the dissolution of the material, but caution is needed, since a high quantity of acid can consume the material instead of aiding the dissolution. Comparing the results of pMC and the time of extraction we can see that a reaction time, between 0:30–1:30 hr, does not add any contamination. This was observed for both samples CA or C2, and the results of pMC are statistically the same. The sample LAC-UFF180329 with a pMC value of 84.32 ± 0.36, clearly shows the presence of some contamination due to bubbles inside the bottle.

The results obtained for C2 samples, as shown in Table 2, are above the IAEA-C2 consensus value (42.43 to 42.7 vs. 41.14); this is probably due to the presence of residual material that was visible at the bottom of the bottle. In order to increase solubility, several steps were tested (shown in Tables 1 and 2), but without success. Casacuberta et al. (2020) also show IAEA-C1 values above the reported from IAEA. They suggest that this is due to the carbon content in the miliQ water and they corrected their blank results with combustion blanks using a combustion step with Cu-Ag. That step allowed reproducing the IAEA-C1 expected value.

This experimental setup with the time of CO_2 extraction set to approximately 30 min and the addition of 1.0 mL of HCl was applied to surface seawater samples, a groundwater sample previously dated at LEMA, and to reference materials. Results are reported in Table 3.

The result of surface seawater showed a value (101.38 ± 0.38) pMC. There are no ^{14}C values reported in the literature for water from the collection area, but Druffel et al. (2016) reported a range of DIC $\Delta^{14}C$ values between +47‰ and +54‰, which correspond to 104.7–105.4 pMC values respectively. These values are reported for surface seawater in the South Atlantic. The result of C2 dissolved in miliQ water and the bicarbonate showed the same value as reported in Tables 1 and 2.

Table 3 pMC values of surface seawater, reference materials (CA and IAEA-C2) and a groundwater sample previously dated. The graphite was analyzed at LAC-UFF.

#IDLAC-UFF	Sample	pMC
180320	Surface seawater (w1)	101.38 ± 0.38
180321	C2 in water	42.83 ± 0.25
180322	bicarbonate	1.22 ± 0.27
180323	LEMA 980	12.91 ± 0.25

The LEMA AMS-Laboratory provided the water sample LEMA 980 from the Instituto de Física, Universidad Nacional Autónoma de México. The average age of 10 replicates was 16,852 ± 100 yr (pMC=12.30 ± 0.15). This sample was kept in the refrigerator until analyzed.

CONCLUSIONS

The results of the AMS analysis in this study of ^{14}C in water demonstrates that LAC-UFF is on the right path for establishing a consistent protocol for water samples. The quantity of 50–60 mL of seawater was enough to obtain enough carbon to make the graphitization. Measurement of blank materials diluted in water showed low values as expected: < 0.4 pMC (> 45,000 ^{14}C yr). The C2 dissolved showed a pMC value of 42.83, value above to IAEA consensus value. Future steps are needed to obtain values closer to those reported by the IAEA. The seawater sample was collected on the surface and a pMC value of 101.4 was found, which is in agreement with values reported in the literature. In addition, the same methodology was used with samples previously dated at LEMA. The results from both laboratories are in agreement.

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