A WET OXIDATION METHOD FOR AMS RADIOCARBON ANALYSIS OF DISSOLVED ORGANIC CARBON IN WATER

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ABSTRACT. We present a method for the extraction of dissolved organic carbon (DOC) from water. The method is adapted from Burr et al. (2001) using the basic steps: 1) sample filtration; 2) acidification to liberate and remove dissolved inorganic carbon (DIC); 3) evaporation of the sample to isolate salts that include trace quantities of carbon; 4) combustion of the salts; and 5) purification of the CO_2. Two significant improvements have been made to the earlier method. The first is to use wet oxidation with potassium permanganate to oxidize organics in place of the combustion step and the second is the development of a reduction/oxidation purification procedure to remove sulfur and nitrogen oxides that may form during the oxidation step. Wet oxidation has a practical advantage over the previous method because it proceeds at low temperature (70 °C). The original method required quartz vessels to oxidize the salts at 900 °C. At this temperature, salts in the samples formed gases that interfered with the isolation of CO_2 and the quartz vessels degraded with each combustion, affecting their structural integrity. The expensive quartz vessels could only be used for a limited number of samples, whereas Pyrex vessels used for wet oxidation are inexpensive and can be used indefinitely.

The blank fraction modern carbon (f) and its mass dependence for the refined technique was determined from repeat analyses of salicylic acid produced from petrochemicals. For samples with a mass m above 0.5 mg, $F = 0.0083 \pm 0.0011$. For samples below 0.5 mg, the blank follows a $1/m$ dependence as observed for other accelerator mass spectrometry (AMS) ^{14}C measurements (Donahue et al. 1990). The reproducibility of the method is demonstrated using repeat measurements from a variety of samples, including a sample measured with the former high-temperature 900 °C combustion technique. The virtues of the wet oxidation method are that it is economical, produces a low blank, and provides good reproducibility.

INTRODUCTION

Measuring the radiocarbon content of dissolved organic carbon (DOC) in groundwater samples, along with dissolved inorganic carbon (DIC), is a proven geochemical tool for understanding the hydrodynamics of an aquifer system (Murphy et al. 1989; Hendry and Wassenaar 2005, 2011; Noseck et al. 2009) and has been applied to freshwater systems from a range of surface environments, including rivers (Raymond and Bauer 2001; Sickman et al. 2010), lakes (Nara et al. 2010a; Zigah et al. 2012), forested catchment areas (Schiff et al. 1997), peatlands (Chasar et al. 2000; Tipping et al. 2010), estuaries (Wang et al. 2007), rainwater (Avery et al. 2006), and sewage effluent (Nara et al. 2010b). A number of different methods can be used to liberate DOC from groundwater for accelerator mass spectrometry (AMS) ^{14}C analysis. Common methods include UV oxidation (Williams and Druffel 1987; Purdy et al. 1992: Raymond et al. 2004), solid phase extraction of various sorts (Murphy et al. 1989; Wassenaar et al. 1990; Sickman et al. 2010), combustion following evaporation and/or freeze-drying (Burr et al. 2001; Palmer et al. 2001; Neff et al. 2006), and ultrafiltration (Thomas 1996; Thomas et al. 1996; Benner et al. 2004). Each of these techniques has its advantages. The UV oxidation approach works especially well in seawater (Druffel et al. 1992; Bauer et al. 1998) where the relatively large proportion of dissolved salts poses a problem for the other techniques. The solid phase extraction and ultrafiltration methods have the virtue that they can be used to distinguish between different classes of organic molecules, according to their molecular weights and chemical characteristics. The direct combustion approach is the simplest method and measures the total DOC in a sample. It requires a minimal sample size, features good reproducibility, and low analytical blanks.

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This study describes in detail the direct combustion technique that is used at the NSF-Arizona AMS Facility. The method is applicable to a wide range of samples, including groundwater samples as small as 500 mL with DOC concentrations as low as tens of μg/L carbon. A primary goal of the study is to quantify the relationship between the magnitude of the blank and sample size. This is known to be significant for AMS samples that contain less than 500 μg C (Donahue et al. 1990).

METHODS

For the blank measurements, the following wet oxidation method was employed: ^{14}C-free salicylic acid was combined with 100 mg granular potassium permanganate ($KMnO_4$) in 1 finger of a 2-fingered glass flask. To the other finger was added 10 mL of phosphoric acid (85%). The flask was subsequently evacuated on a high-vacuum line and sealed via a valve fixed to the top of the flask. The evacuated sealed flask was then detached from the vacuum line and tipped at an angle in order to pour the phosphoric acid into the finger with the salicylic acid-potassium permanganate mixture. The sample was then heated to 70 °C on a heat block overnight (minimum of 10 hr). When the reaction was completed, the sample flask was fixed to a high-vacuum line, and the CO_2 gas produced from the reaction was allowed to bleed through 2 isopropanol-dry ice traps and 1 liquid nitrogen trap. To minimize isotopic fractionation of the gas, the pressure in the cold trap was maintained below 10^{-1} Torr while bleeding. Once the vacuum in the line reached 10^{-5} Torr or better, the sample was isolated using another liquid nitrogen cold trap, then subsequently expanded into a known, measured volume in order to calculate the volume of CO_2. The sample was then collected in a sample vessel and submitted for ^{13}C and ^{14}C analyses. Flask clean-up involved rinsing with hot concentrated HCl followed by purified water.

This sample preparation method was replicated numerous times and the sample sizes covered a range from 20 to 500 μg. Additionally, standard samples were also tested, using oxalic acid I standard, with a theoretical yield of about 1 mg. Once the blank was established, the method was used to process groundwater samples. The samples were first filtered through a 0.7-μm glass microfiber filter fixed to a 500-mL Nalgene container with a hand-operated vacuum pump. It is possible to utilize a 0.45-μm nylon filter if proper washing techniques are employed to remove contaminants; however, for the purposes of this study and avoidance of carbon contamination, the 0.7-μm glass microfiber filter was chosen. The filtered sample, ~1.0 L, was then transferred to a large, round-bottomed flask and 20 mL of phosphoric acid (85%) was introduced into the flask. The vessel was then fixed to an evaporation system (Figure 1) and heated to 40 °C while under a vacuum of 10^{-2} Torr. The temperature was maintained at 40 °C to avoid losing volatile organic compounds. During this heating period, the water evaporated from the sample was frozen in an isopropanol-dry ice trap, cooled with a chiller unit (Figure 1), and the dissolved organic carbon was left behind, along with dissolved salts suspended in the phosphoric acid. The evaporation step took up to 3 days to complete.

After the sample was evaporated, the reaction flask was chilled in an ice bath, brought up to atmosphere, and 150 mg of potassium permanganate was added to the flask. The sample-phosphoric acid mixture in the flask is very hygroscopic and an inert gas (e.g. N_2 or Ar) should be used to bring the pressure in the vessel up to atmosphere, before adding the potassium permanganate. Following this step, the flask was pumped down to 10^{-2} Torr and isolated from the vacuum system. The sample flask was then heated to 70 °C overnight to allow the reaction to proceed. Next, the flask was attached to a high-vacuum line and the CO_2 gas produced from the reaction was bled through 2 isopropanol-dry ice traps and 1 liquid nitrogen trap (Figure 2). A modification adopted during the development of this procedure was to place the sample vessel in a large isopropanol-dry ice bath, to provide an additional water trap. As in the earlier procedure, the CO_2 is passed through 2 additional cold traps and collected as a solid in a liquid nitrogen cold trap. The CO_2 is then allowed to subli-

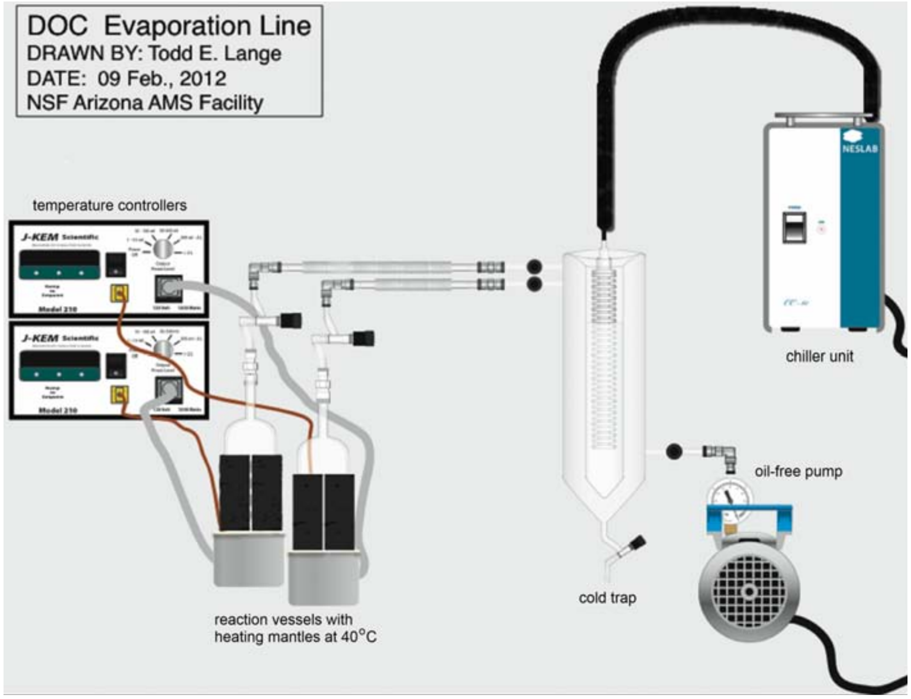

Figure 1 DOC evaporation and reaction vacuum line. This line can accommodate 2 samples at the same time.

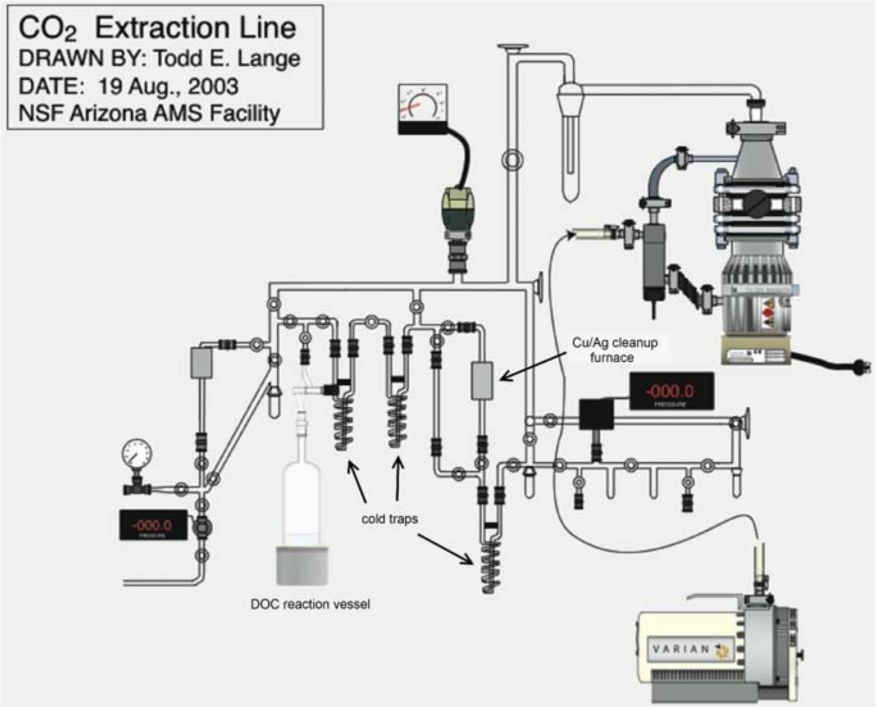

Figure 2 DOC - CO_2 collection and purification vacuum line

mate and expand into an area of the vacuum line containing a copper/silver reduction furnace to purify it (Figure 2). Any reducible contaminate gases are removed once the pressure in the line has stabilized. The sample is then transferred into a known, measured volume section of the vacuum line in order to calculate the mass of CO_2. Once collected in a sample vessel, the CO_2 was then analyzed for $\delta^{13}C$ using a conventional isotope ratio mass spectrometer and for ^{14}C by AMS. The sample flasks used in the above preparation method can be used repeatedly after cleaning.

Gas Purification

For high sulfur groundwater samples, a reduction oxidation clean-up method was utilized to remove SO_2. This step was taken because SO_2 can inhibit the formation of graphite during the reduction reaction. The presence of SO_2, and possibly nitrogen oxides, are sometimes obvious from the behavior of the sample on the vacuum line. Symptoms include 1) very slow transfer rates as gas is moved from one cold trap to the next; 2) unstable pressure readings after the gas has been frozen into a cold trap; and 3) visible coloration in samples frozen in liquid nitrogen. We routinely confirm these observations with stable isotope measurements on a conventional mass spectrometer. Spectral traces of such samples typically show wide or irregular patterns instead of sharp peaks for each isotope. The method we developed produces sequential reduction/oxidation reactions in a single vessel. The idea is to reduce the CO_2 and contaminating gases and then re-oxidize the CO_2. From repeated experiments, we found that once reduced, the contaminating gases do not readily re-oxidize and are therefore removed. The technique uses Zn to reduce the gases and CuO to oxidize them. We are able to perform the reaction in a single tube because the reduction and oxidation steps occur at different temperatures, and the reduction temperature is significantly lower than the oxidation temperature. The clean-up procedure procedes as follows: 1) CO_2 and contaminating gases are transferred to a quartz tube containing 10 mg of Zn and 150 mg of CuO; 2) the sample is frozen in liquid nitrogen and any residual gas is pumped away as the tube is sealed off with a torch; 3) the tube is heated in an oven to 450 °C for 2 hr to reduce the gases and then to 800 °C for 2 hr to re-oxidize CO_2. At this stage, the gas has been purified. After the tube has cooled, it is placed in a tube-cracker on the high-vacuum line and the CO_2 volume is measured. This method has worked for all freshwater samples that we have processed in the laboratory; however, when used on seawater the salt content was found to be too high to effectively remove the contaminating gases.

RESULTS AND DISCUSSION

The results of the AMS analyses are given in Table 1. These include results for salicylic acid blanks, oxalic acid standards, tap waters, and a groundwater sample analyzed using both the former method (oxidation at 900 °C) and the current (wet oxidation) technique (measured 3 yr apart). The repeat measurement on the groundwater sample agreed well with the original measurement (Table 1). By pooling the remaining repeat samples (3 oxalic acids and 3 tap waters), we calculate a reproducibility of 3‰, at a 1σ confidence level.

The salicylic acid manufactured from petrochemicals was used to quantify our DOC blank and its mass dependence. The data are given in Table 1 and are plotted in Figure 3, as blank fraction modern carbon (f) values. No mass correction or ^{13}C correction has been applied to these results, and only counting statistics are reported. Samples with very small masses (<100 μg) show a sharp rise in f as their carbon mass (m) decreases. We also observe increased scatter in the results as we approach the sample size limit of the technique. This observed trend is consistent with a small but relatively constant amount of contaminant that is introduced into the sample during processing to graphite and is characteristic of AMS samples. That is, we can assign a $1/m$ blank-mass relationship as $f(m) = f(1mg)/m$ (Donahue et al. 1990) for samples <500 μg. We estimate our DOC groundwater blank to be f (1 mg) = 0.0083 ± 0.0011. The red line in Figure 3 shows this value as it follows the 1/*m* trend. When using this blank relationship, it is clear that the uncertainty of a measurement will increase as the mass of a sample decreases, for samples <500 μg. In practice, this is quantified by expanding the error envelope for the very small samples, and propagating the blank error into the total uncertainty for a measurement.

Table 1 AMS ^{14}C results with ±1σ counting uncertainties. f is the uncorrected fraction modern carbon (with no blank or ^{13}C correction) and F is the fraction modern carbon (Donahue et al. 1990).

Lab code	Lab #	Mass (mg)	δ^{13}C (‰)	f
Salicylic acid blanks				
AA88186	X19351	0.02	–27.6	0.0624 ± 0.0026
AA88187	X19352	0.04	–27.5	0.0417 ± 0.0016
AA95763	X21082	0.04	–24.4	0.2580 ± 0.0017
AA95762	X21081	0.05	–23.7	0.2340 ± 0.0017
AA88190	X19355	0.05	–25.2	0.0887 ± 0.0020
AA88188	X19353	0.07	–25.2	0.0708 ± 0.0013
AA95765	X21084	0.07	–24.3	0.1434 ± 0.0011
AA93954	X19474	0.08	–24.8	0.0828 ± 0.0015
AA94705	X20310	0.09	–24.8	0.0854 ± 0.0006
AA95764	X21083	0.09	–25.1	0.1658 ± 0.0011
AA93950	X19470	0.10	–24.9	0.0585 ± 0.0010
AA95766	X21085	0.10	–25.0	0.1183 ± 0.0009
AA88189	X19354	0.12	–25.5	0.0541 ± 0.0009
AA93952	X19472	0.12	–24.8	0.0508 ± 0.0006
AA94165	X19746	0.13	–24.5	0.0628 ± 0.0007
AA93953	X19473	0.16	–25.1	0.0387 ± 0.0005
AA95044	X20472	0.17	–24.4	0.0604 ± 0.0007
AA95045	X20473	0.17	–24.5	0.0642 ± 0.0007
AA95046	X20474	0.17	–24.0	0.0577 ± 0.0007
AA93951	X19471	0.20	–24.9	0.0426 ± 0.0005
AA94258	X19871	0.23	–24.9	0.0393 ± 0.0007
AA94706	X20311	0.23	–25.0	0.0303 ± 0.0005
AA94166	X19747	0.33	–25.0	0.0260 ± 0.0004
AA94167	X19748	0.39	–24.8	0.0199 ± 0.0004
AA94168	X19749	0.47	–25.0	0.0196 ± 0.0004
Oxalic acid standards				
Lab code	Lab #	Mass (mg)	^{13}C (‰)	F
AA95767	X21086	0.74	–18.8	1.0226 ± 0.0042
AA95768	X21087	0.84	–18.8	1.0314 ± 0.0042
AA95769	X21088	0.87	–18.8	1.0264 ± 0.0042
Tap water samples				
AA86253	X15251	0.45	–24.0	0.5604 ± 0.0035
AA86254	X15389	0.37	–21.9	0.5603 ± 0.0039
AA86255	X15432	0.34	–21.7	0.5765 ± 0.0042
Groundwater (both are Barcass D24)[a]				
AA70681	X4784	0.11	–26.5	0.5213 ± 0.0069
AA86249	X14345	0.33	–23.4	0.5291 ± 0.0065

[a] AA70681 was combusted in oxygen at 900 °C in August 2006. AA86249 is from the same well and was processed with the wet oxidation method in August 2009.

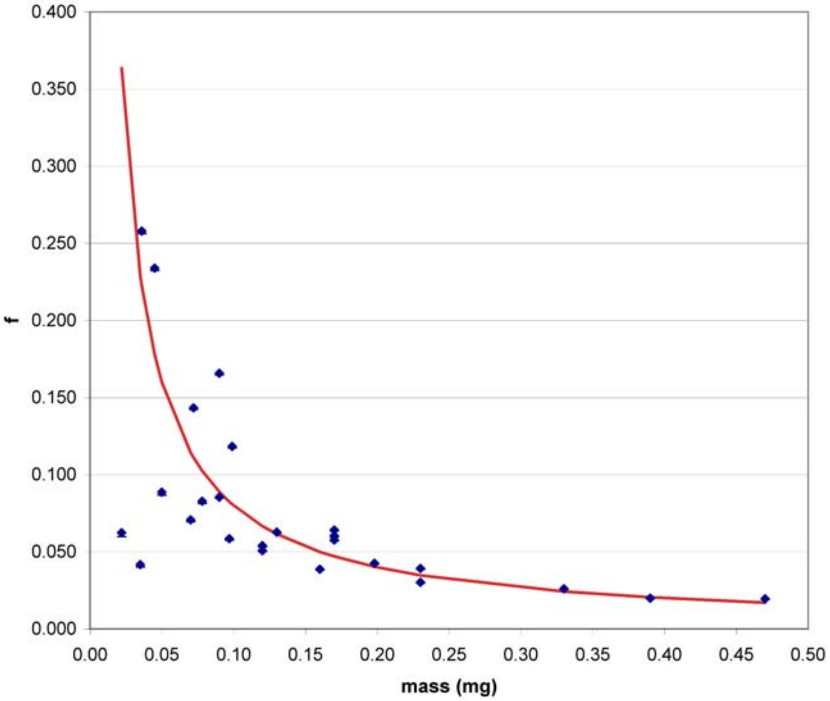

Figure 3 Blank fraction modern carbon (*f*) values measured for different sample masses. The blue points are the raw data, with no blank correction or ^{13}C correction applied. The red line shows the 1/*m* dependence of the blank for samples below about 0.5 mg C.

We surveyed the recent literature to compare our technique with others being used to measure ^{14}C in freshwater DOC samples by AMS. Table 2 is not an exhaustive list, but gives a fair cross-section of methods employed in different studies. It shows that there are 4 primary methods for such analyses: 1) drying and combustion (as in this study); 2) solid phase extraction (SPE) using resins of various sorts and other solid reactive materials; 3) UV oxidation; and 4) ultrafiltration. Although many of the studies listed in Table 2 discussed the overall blank for their samples, no other study specifically addressed the relationship between the sample mass and blank. Our interest in quantifying this relationship is to allow us to establish a lower limit for sample size, to correct for sample results that contain different amounts of carbon where appropriate, and to assign the uncertainty from the blank correction in a measurement, associated with a particular sample. The data presented here allows us to do that.

There are a number of differences between DOC measurements made with different techniques. As noted above, for example, the SPE and ultrafiltration methods provide information on specific DOC molecular groups, according to their molecular weights or chemical characteristics, but not total DOC. The UV method targets DOC that can be oxidized by irradiation with a UV light source. Extensive seawater analyses suggest that the UV technique captures all of the DOC (Bauer et al. 1998) and the combustion method also provides a result for total DOC. Given these differences, one should take care when comparing DOC data that have been measured using different techniques. This is true even in the case where 2 studies use the same method because DOC is operationally defined as dissolved organics that pass through a specific filter size, and the filter sizes used in the various studies quoted in Table 2 range for 0.2 to 0.8 μm.

Table 2 Survey of DOC extraction methods employed in the recent literature for AMS DOC analyses of freshwater samples. Four common methods are 1) combustion following drying (freeze-drying or evaporation); 2) solid phase extraction (SPE), using resins or other solid reactants in a column; 3) UV oxidation; and 4) ultrafiltration.

DOC sample preparation method(s)	References
Dry and combust	Schiff et al. 1997; Palmer et al. 2001; Benner et al. 2004; Karltun et al. 2005; Neff et al. 2006; Evans et al. 2007; Tipping et al. 2007, 2010; Noseck et al. 2009; Nara et al. 2010a,b
SPE	Murphy et al. 1989; Hendry and Wassenaar 2003; Benner et al. 2004; Sickman et al. 2010
UV oxidation	Purdy et al. 1992; Bauer et al. 1998; Raymond and Bauer 2001; Chasar et al. 2000; Raymond et al. 2004; Avery et al. 2006; Baker et al. 2011; Zigah et al. 2012
Ultrafiltration	Thomas 1996; Thomas et al. 1996; Benner et al. 2004; Wang et al. 2006

CONCLUSIONS

We present a pretreatment and processing technique for isolating DOC from freshwaters for AMS ^{14}C analysis. The method is simple and inexpensive, and produces low blanks and good reproducibility. The method is modified from the direct combustion technique of Burr et al. (2001), substituting wet oxidation for high temperature combustion. The wet oxidation technique allows us to use relatively inexpensive Pyrex reaction vessels that can be used indefinitely. Although the technique is time consuming, it is less labor-intensive that the previous technique. In addition, we have devised a gas clean-up technique that is effective in removing SO_2 and other contaminants from the gas produced during the wet oxidation of freshwater samples. We estimate our current DOC groundwater blank to be f (1 mg) = 0.0083 ± 0.0011, and we show that the blank increases as sample mass decreases below 500 µg, with a $1/m$ dependence.

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