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RADIOCARBON IN DISSOLVED ORGANIC CARBON BY UV OXIDATION: AN UPDATE OF PROCEDURES AND BLANK CHARACTERIZATION AT NOSAMS

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ABSTRACT. This note describes improvements of UV oxidation method that is used to measure carbon isotopes of dissolved organic carbon (DOC) at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS). The procedural blank is reduced to $2.6 \pm 0.6 \mu\text{g C}$, with F_m of 0.42 ± 0.10 and $\delta^{13}\text{C}$ of $-28.43 \pm 1.19\text{‰}$. The throughput is improved from one sample per day to two samples per day.

KEYWORDS: blank, dissolved organic carbon, radiocarbon, UV-oxidation.

INTRODUCTION

Dissolved organic carbon (DOC) represents a large and reactive carbon reservoir in aquatic systems. Radiocarbon (^{14}C) measurements in DOC provide key insights into the age and geochemical cycling mechanisms of this important global carbon reservoir. A recent paper documented the procedures utilized for DOC radiocarbon measurements at the National Ocean Science AMS facility (NOSAMS; Xu et al. 2021). A major component of that paper was to characterize the procedural blanks and to describe modifications to the procedures intended to minimize blank contributions. In that effort, the DOC UV oxidation blank was reduced from $22 \mu\text{g C}$ to $11 \mu\text{g C}$. This note describes some recent modifications to the procedure, described by Xu et al. (2021), that further reduces the blank to $2.6 \pm 0.6 \mu\text{g C}$ and doubles the throughput.

METHOD

The method is basically the same as that in Xu et al. (2021) with several procedural changes. The most notable change relates to handling and exposure of the water-cooling probe: After the UV pretreatment of Milli-Q water (for standards, blanks, and small volume samples), the water-cooling probe is now placed in a cylindrical glass container with 65/40 socket filled with fresh Milli-Q water (Figure 1, right). Previously, the wet water-cooling probe was held by a clamp on a stand, exposed to laboratory air (Figure 1, left). At this time, a standard solution (about 2 mL) or a small volume sample and 0.4 g 33% ultra-pure hydrochloric acid are added to the quartz reactor.

To improve sample throughput, we built a new UV oxidation chamber using a stainless-steel barrel (0.76 m diameter, 0.96 m height, 1.2 mm thickness). This larger chamber allows two (potentially three) reactors to be placed in the chamber at the same time with a single UV lamp. The UV reflector described in Beaupre et al. (2007: their Fig. 4) was removed with no loss of efficiency. Two “T” splitters (crosses for three reactors) and plug valves were installed for the gas inlet and outlet. The same modification was done for cooling water.

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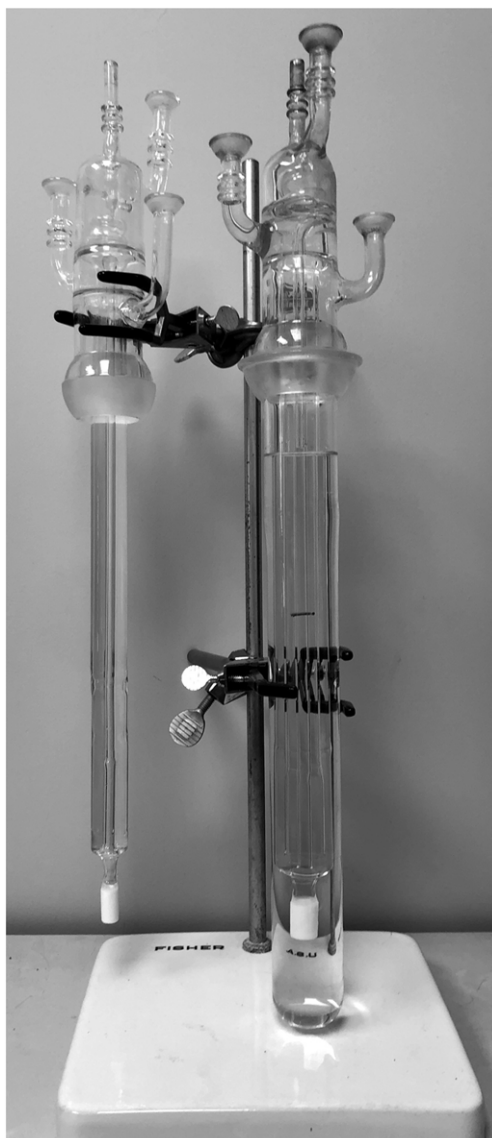


Figure 1 The DOC water-cooling probe used at NOSAMS. At left, the water-cooling probe is exposed to air. At right, the water-cooling probe is stored in a glass container with 65/40 socket filled with fresh Milli-Q water. Storage of the cooling probe in water (right), instead of air, is the main procedural change described here, resulting in lower blanks.

DIC can be purged off simultaneously from the two oxidation reactors, and two samples can be UV oxidized at the same time. At the end of the UV oxidation, the CO_2 from DOC is extracted sequentially/separately for each sample.

Another procedural modification, compared to the Xu et al. (2021) paper: the halogen trap, previously using a potassium iodine solution, was replaced with a copper wool flow-through

trap (glass u-tube). The replacement eliminates the possibility of pumping potassium iodide solution into the vacuum section of the DOC line and facilitates leak checking.

We analyzed a series of blanks (direct method), and a series of prepared standards (OX-II and glycine) of varying mass (indirect method, using comparison of Fm to an accepted value), to estimate the process blank as described in Xu et al. (2021).

RESULTS

The “direct” blank was measured using Milli-Q water with the latest protocol; the amount of blank carbon produced was measured by manometry and sealed in 6 mm OD glass tubes. Five to ten blanks were pooled for AMS radiocarbon ^{13}C measurements by IRMS to determine fraction modern and $\delta^{13}\text{C}$ of the blank. Direct blanks ranged from 1.2 to 4.7 $\mu\text{g C}$, with a mean of $2.3 \pm 0.6 \mu\text{g C}$ ($n=29$). For comparison, the direct blank in Xu et al. (2021) was $6.7 \pm 3.6 \mu\text{g C}$. The Fm was 0.44 ± 0.070 ($n=4$), and $\delta^{13}\text{C}$ was $-28.43 \pm 1.19\text{‰}$ ($n=4$). The indirect measurement of the blank was obtained by AMS radiocarbon analysis of secondary standards OX- II (SRM 4990C), and Sigma Aldrich Glycine, run through the entire DOC procedure, as shown in Figure 2. The modeled estimate for the procedural blank is $2.6 \pm 0.6 \mu\text{g C}$, with Fm of 0.42 ± 0.10 . The previous values were $11.0 \pm 2.75 \mu\text{g C}$ with Fm = 0.14 ± 0.10 , which is a significant reduction. The direct and indirect measurement of process blank agree well ($2.3 \pm 0.6 \mu\text{g C}$, Fm 0.44 ± 0.070 and $2.6 \pm 0.6 \mu\text{g C}$, Fm 0.42 ± 0.10 , respectively).

For the new setup, it is now possible to process two DOC samples per day, doubling the previous throughput of one sample per day. The daily working time for two samples is 1.5 hr longer to load and extract the second sample, compared to the previous single sample procedure. The yield of standards (OX-II and glycine) ranged from 93 to 102% with an average of $99 \pm 3.6\%$, $n=23$, for masses ranging from 22 $\mu\text{g C}$ to 792 $\mu\text{g C}$. Blanks using the two-reactor setup are indistinguishable from the single reactor setup.

CONCLUSION AND IMPLICATION

To reduce exposure to laboratory air, the glass water-cooling probe used in the DOC UV oxidation reactor was stored in Milli-Q water after the UV-pretreatment of water, while samples/standard and acid are being added. This simple modification to the procedure described by Xu et al. (2021) reduced the DOC method blank significantly. Based on the decrease in the blank size (from 11.0 to 2.6 $\mu\text{g C}$), and increase in Fm, we infer that this procedure minimizes contributions from gaseous organic material in the laboratory air. The most likely contribution is isopropanol, which is extensively used throughout the sample preparation laboratory, but we cannot exclude other contributions. Isopropanol is volatile and water soluble and would be easily absorbed onto the wet surface of the water-cooling probe. Xu et al. (2013) observed that baked quartz filter would absorb organic material over time and that the Fm of the blank decreased with time. They attributed this to the old volatile organic carbon in the lab air. Based on the improved DOC blanks reported here, we infer that DOC samples, and wet glassware, should be handled in an organic free lab or laminar hood, or with limited exposure to laboratory air, to minimize contamination from volatile organic compounds in laboratory air.

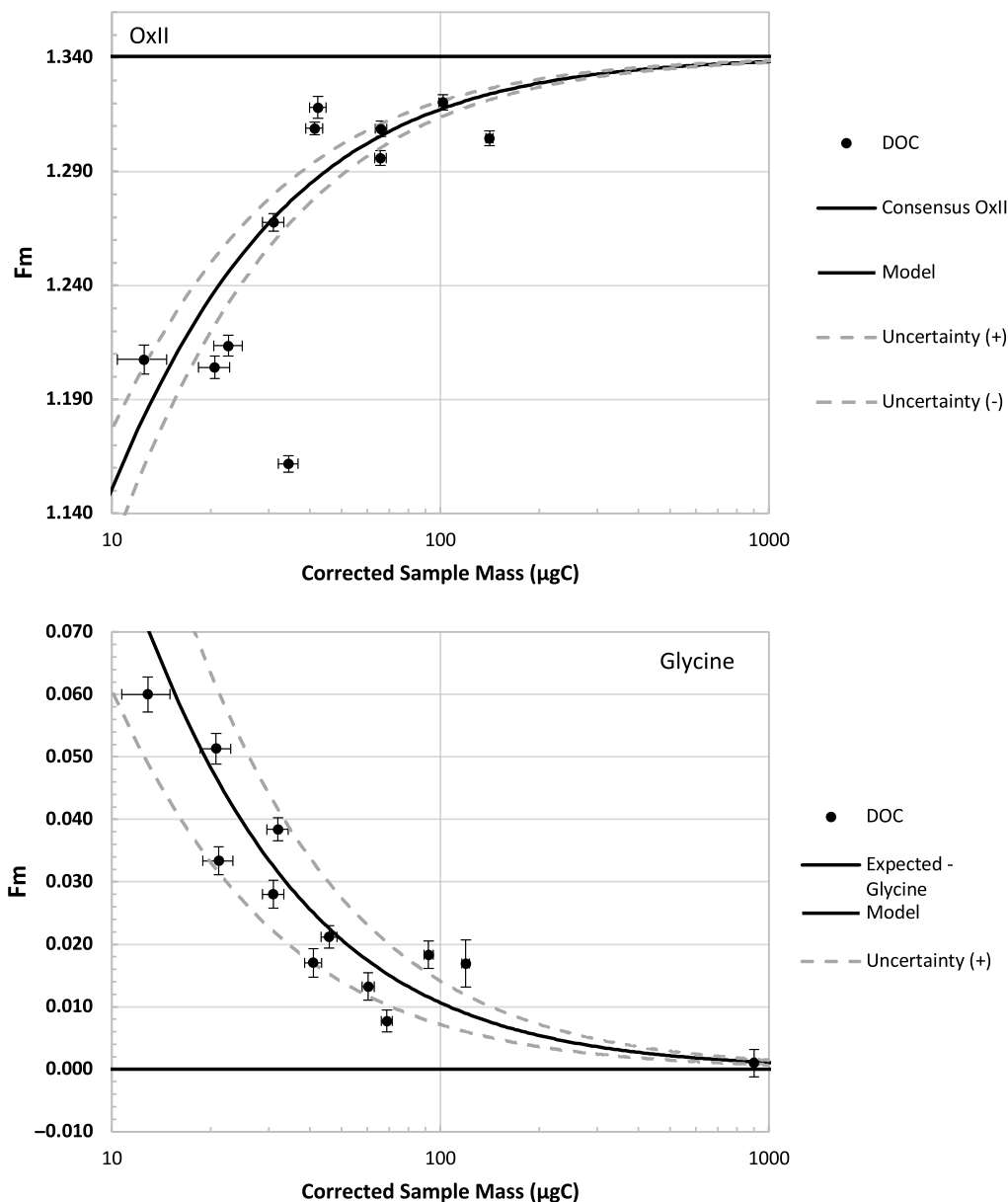


Figure 2 Compilation of F_m (fraction modern ^{14}C) for two secondary standards, OX-II and glycine, as a function of mass, all of which processed using the newly modified DOC procedure. The horizontal lines in each diagram represent the accepted values for each material; OX-II and glycine. The curves represent the best estimate for impact of a blank of $2.6 \pm 0.6 \mu g C$ with $F_m = 0.42 \pm 0.10$.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the U.S. National Science Foundation, via NSF-OCE-1755125. We thank the entire NOSAMS staff for assistance, and Colin Ward, Chris Reddy, and Ulrich Hanke for discussions and encouragement.

REFERENCES

- Beaupré SR, Druffel ERM, Griffin S. 2007. A low-blank photochemical extraction system for concentration and isotopic analyses of marine dissolved organic matter. *Limnology and Oceanography: Methods* 5:174–184. doi: [10.4319/lom.2007.5.174](https://doi.org/10.4319/lom.2007.5.174).
- Xu L, Roberts ML, Elder KL, Kurz MD, McNichol AP, Reddy CM, Collin CP, Hanke UM. 2021. Radiocarbon in dissolved organic carbon by UV oxidation: procedures and blank characterization at NOSAMS. *Radiocarbon* 63(1):357–374. doi: [10.1017/RDC.2020.102](https://doi.org/10.1017/RDC.2020.102).
- Xu X, Gao P, Salamanca EG. 2013. Ultra small-mass graphitization by sealed tube zinc reduction method for AMS ^{14}C measurements. *Radiocarbon* 55(2):608–616.