THE PREPARATION OF WATER (DIC, DOC) AND GAS (CO₂, CH₄) SAMPLES FOR RADIOCARBON ANALYSIS AT AEL-AMS, OTTAWA, CANADA

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ABSTRACT. Sample preparation techniques for radiocarbon analysis of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in freshwater, as well as CO_2 and CH_4 in gas mixtures are presented. Focused efforts have been on developing a robust and low-background wet oxidation extraction method for DOC in freshwater, following routine methods developed for stable carbon isotope analysis and adapted for radiocarbon (^{14}C) analysis. DIC (by acidification) and DOC (by wet oxidation) are converted to CO_2 in pre-baked septum-fitted borosilicate bottles, where the resulting CO_2 is extracted from the dissolved and headspace portions on a low-flow He-carrier flow-through system interfaced to a vacuum extraction line. A peripheral CH_4 extraction line interfaces to the flow line to separate CH_4 from environmental samples following the methods of Pack et al. 2015. High sample throughput and low blanks are achievable with this method. DIC and DOC blanks are consistently <0.7 pMC, while CO_2 and CH_4 blanks are typically <0.1 pMC.

KEYWORDS: DIC, DOC, flow-through system, gas mixtures, wet chemical oxidation.

INTRODUCTION

The A. E. Lalonde AMS Laboratory (AEL-AMS) has been in operation since 2014, providing routine radiocarbon (^{14}C) analysis of a wide range of organic and inorganic materials (Crann et al. 2017). The radiocarbon content of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in freshwater systems, as well as CO_2 and CH_4 in gas mixtures, provides insights on carbon cycling dynamics and source apportionment in environmental systems (Lachinet et al. 2012; Mann et al. 2015; Grinter et al. 2018; Wang et al. 2018). To meet increasing demand, a method development program has been undertaken to improve sample preparation techniques for greater precision and to accelerate processing of water (DIC, DOC) and gas (CO_2, CH_4) samples at AEL-AMS, particularly for dissolved organic carbon (DOC) in water. Wet chemical oxidation has commonly been employed for stable isotope analysis of $DO^{13}C$ in waters (St-Jean 2003; Osburn and St-Jean 2007; Lang et al. 2012; Zhou et al. 2015, etc.), and more recently has been applied to ^{14}C (Leonard et al. 2013, Lang et al. 2016). Other methods such as UV oxidation (Beaupre et al. 2007; Druffel et al. 2013), evaporation and lyophilization (Burr et al. 2001; Neff et al. 2006) and solid phase extraction techniques (Sickman et al. 2010; Hendry and Wassenaar 2005) are limited by complicated analytical routines and long processing times, where high temperature catalytic oxidation (HTCO) methods generally report high analytical blanks (Hedges et al. 1993; Benner and Strom 1993). Focused efforts have been on developing a robust DOC extraction method by wet oxidation for freshwater samples designed specifically for high throughput. Extraction protocols for gas samples (CO_2 and CH_4) at AEL-AMS are also discussed.

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Table 1 Standard reference material for AEL-AMS material codes.

Material Code	Standard ID	Material	Type	pMC (expected)	pMC (average)
DIC	NaHCO$_3$	Sodium bicarbonate*	Process blank[1]	~0	0.55 ± 0.02
	IAEA-C2	Travertine*	Secondary ref.[2]	41.14	41.06 ± 0.25
DOC	kHP	Potassium hydrogen phthalate*	Process blank[1]	~0	0.44 ± 0.02
	SWRNOM	Suwannee River natural OM*	Modern ref.[1]	106.18	106.12 ± 0.32
	OXII	Oxalic Acid II*	Modern ref.[2]	134.07	132.61 ± 0.45
CX	Air Liq-CO$_2$	^{14}C-free CO$_2$ gas	Process blank[1]	~0	0.07 ± 0.01
CH4	Air Liq-CH$_4$	^{14}C-free CH$_4$ gas	Process blank[1]	~0	0.08 ± 0.01

*Dissolved in 20 mL of ultra pure Milli-Q water.
[1]Independently verified by direct combustion (organics) or hydrolysis (inorganics).
[2]Consensus value.

METHODS

Samples are assigned a lab identifier number (UOC-#) and processed according to media codes based on the analysis of interest (Table 1). Appropriate reference materials are processed with each batch of unknowns, also summarized in Table 1. Concentration information (ppmC) is requested at the time of submission to determine the appropriate volume of material required to yield ~1.0 mgC for ^{14}C analysis.

DIC and DOC

Definitions of what constitutes DIC and DOC can vary depending on the user and field of study; typical designations of what represents carbon species in aqueous systems can be found in St-Jean (2003). At the AEL-AMS lab, water samples are requested to be received pre-filtered with baked (500ºC for 3 hr) 0.7-µm GF/F filters or pre-rinsed 0.45-µm nylon or polypropylene filters, depending on the application; these filters were tested to have slightly lower blank contributions (<1 pMC) compared with nitrocellulose (>1.5 pMC). Round-bottom borosilicate Wheaton® bottles (Cat. No. 219439) are used as the reaction bottles for both DIC (by acidification) and DOC (by wet chemical oxidation) extractions. All bottles are pre-cleaned (10% HCl, MilliQ rinse), pre-baked (500ºC for 3 hr) before each use, and are reusable. Bottles are capped with a pre-cleaned (10% HCl, sonicate in MilliQ, dried at 50ºC overnight) butyl septum closure (33-430, Wheaton Cat. No. 240680). The appropriate bottle size (125 mL, 250 mL, 500 mL or 1000 mL) is selected based on the volume of water required (depending on concentration) to yield ~1.0 mgC, and to leave a minimum of 1/3 headspace volume so as to not overpressure the reaction bottle during the extraction.

For DI^{14}C analysis, the required volume of water is transferred via septum cap using a double-ended needle or by syringe into a pre-evacuated ($<10^{-2}$ mbar) reaction bottle with 3–5 mL of 85% o-phosphoric acid to acidify the sample to pH <2. The sample bottle is then heated on a hot plate to 60°C for 1 hr to convert all dissolved inorganic species to CO_2 into the headspace. The bottles are allowed to cool to room temperature prior to CO_2 extraction.

For DO^{14}C analysis, the water sample is transferred into an appropriate sized reaction bottle leaving at least 1/3 headspace to avoid overpressure. The sample is acidified to pH <2 with 85% o-phosphoric acid via open cap and sparged with He for 15 min. The reaction bottles are then capped and heated to 60°C for 1 hr. Following heating, the headspace is sparged a second time with He through the septa to remove any residual DIC fraction, and the sample is cooled to 4ºC. The DOC fraction is then oxidized to CO_2 following a wet chemical oxidation (WCO) technique modelled after St-Jean (2003); Lang et al. (2012, 2016) and Zhou et al. (2015). A stock of oxidant solution is prepared by dissolving 400g $Na_2S_2O_8$ (Sigma Aldrich >99% purity, Cat. No. 71890) in 1L boiling MilliQ water for 5 min to clean the oxidant and reduce the blank. A fixed volume of oxidant solution (8 mL) is added to the cold DIC sparged sample via the septa along with 1 mL of 0.5N $AgNO_3$ (Fisher Scientific, Cat. No. S181) which acts as a catalyst to improve CO_2 yield (Zhou et al. 2015). The volume of oxidant remains constant as all samples (of varying ppmC concentrations) are portioned volumetrically to ultimately target a fixed amount of carbon (1 mgC). The amount of oxidant added is a minimum of 10$\times$ excess for what is needed to convert 1 mg of organic carbon to CO_2, to account for (1) loss of oxidation power during heating of the oxidant solution, (2) recalcitrant organic carbon that is difficult to oxidize, and (3) dissolved ions in solution competing for the $Na_2S_2O_8$. The bottle is heated to 95°C for 60 min on a hotplate with occasional gentle manual swirling, then allowed to cool to room temperature prior to CO_2 extraction.

Once the sample is reacted, CO_2 is extracted from the headspace on a low-flow He carrier extraction line (discussed below).

CX (CO_2 Extraction and Purification)

CO_2 is extracted from the headspace of the reaction bottle (for DIC/DOC) or a thick butyl rubber septum-fitted Wheaton® bottle (for CX) on a multipurpose extraction line. The line consists of stainless steel and PEEK tubing for the Helium (He) carrier flow-through section (Figure 1A) interfaced to a glass vacuum line for subsequent purification and trapping of CO_2 in a breakseal (Figure 1B).

The flow-through section (A) sweeps CO_2 from the headspace of the reaction bottle using a He carrier gas, regulated at 200 mL/min (1). This section of the line consists of two 20-gauge stainless steel needles which are inserted through the septum of the reaction bottle: a 12-inch-long sparging needle (2) that bubbles He through the water sample, and a 6-inch exit needle (3) into the headspace which completes the flow conduit through the reaction bottle. The carrier section is equipped with a Nafion™ (Permapure MD-070-96P-2) gas dryer (4), designed to remove traces of water from the carrier (He) and extracted CO_2, which are impermeable to the membrane and continue through to a stainless steel U-trap (5) packed with Ag wool (to increase surface area). This trap is immersed in liquid nitrogen (LN$_2$), where CO_2 freezes and He vents to atmosphere. The reaction bottle headspace is flushed by 10x its volume to ensure all CO_2 is removed.
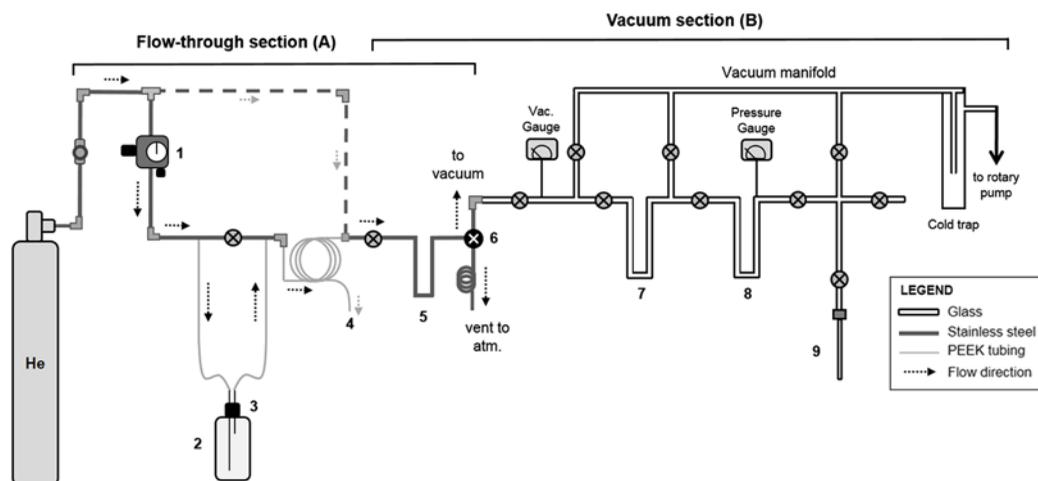
Figure 1 Schematic diagram of multipurpose line for extraction of waters (DIC/DOC) and CO_2 (CX) samples, showing (A) flow-through section and (B) vacuum section. Numbers are described in the text.

The flow section is interfaced to a vacuum line (B) via a three-way valve (6) with a port to *vent* and the other to *vacuum*. Once the extraction is complete, the stainless-steel U-trap (5) is isolated on both sides, and the flow of He is immediately shut off (NB: this is a critical step to prevent over pressuring the carrier section and damaging the Nafion™ membrane). Helium and other non-condensable gases are evacuated from the U-trap volume while the CO_2 remains frozen at LN_2 temperature. The vacuum is then isolated from the manifold, a –80°C ethanol bath is placed on the stainless-steel U-trap (5) to release CO_2 and hold any residual water, and the extracted CO_2 is transfered through to the vacuum section for cryogenic purification on a glass U-trap (7). The purified CO_2 is then quantified in a calibrated volume (8) using a Baratron gauge. The measured CO_2 is then transferred to a pre-baked (500°C for 3 hr) 6-mm OD borosilicate breakseal (9) containing a small amount (5–6 grains) of Silvered Cobaltous/Cobaltic oxide (Elemental Microanalysis, Cat. No. B1120) which has been previously baked at 500°C for 2 hr. The breakseal is sealed with the CO_2 sample and baked at 200°C overnight to remove any S-bearing species that may poison the Fe catalyst during graphitization (Palstra and Meijer 2014).

CH$_4$

Methane samples are processed on a high temperature oxidation line following the methods of Pack et al. (2015), which is interfaced to the multipurpose vacuum extraction line (not shown in Figure 1) connected to the left of the stainless steel U-trap. In summary, CH_4 in headspace is sampled from a septum capped bottle via gas-tight syringe that is pre-flushed with He to eliminate atmospheric CO_2 contamination. The sample is injected slowly (<100 mL/min) via septum fitting and needle valve into a flow-through vacuum oxidation line with a carrier of ultra-zero compressed air (UZ air). Maintaining a low injection flow is critical to ensuring the efficiency of the traps and combustion of methane (Pack et al. 2015). The carrier is purified with an in-line CO_2 trap (EMASorb A, Elemental Microanalysis B1115) and held at a flow rate of 10 mL/min through the line. CO_2 and water are preliminarily removed from the sample on a dual chemical trap consisting of EMASorb A and Magnesium Perchlorate mixed with 1/3 Quartz chips (Elemental Microanalysis, B1019 + B1271). This is

followed by cryogenically trapping of residual CO_2 and water from the sample on a LN_2 trap. CO is removed on a subsequent trap consisting of a 290°C oven packed with CuO rods (Fisher Scientific, C474) to oxidize CO to CO_2, followed by a second LN_2 trap. Methane is combusted to CO_2 in a 975°C tube furnace packed with CuO rods (regenerated by the constant flow of UZ air) and Silvered Cobaltous/Cobaltic oxide towards the bottom of the reactor to remove S-bearing species and halides. Any water produced from the combustion is separated from the CO_2 on a −80°C trap, and the CO_2 from the methane combustion is trapped on a final LN_2 trap. Following complete combustion of the sample (∼10 min), the purified CO_2 is transferred to the vacuum section of the line (Figure 1B) and sealed in a breakseal.

Graphitization and AMS Analysis

Following CO_2 purification, all samples are converted to graphite by hydrogen reduction on custom-build semi-automated graphitization lines (see St-Jean et al. 2017). Graphite samples are pressed into sample targets and subsequently analyzed on a 3MV tandem accelerator mass spectrometer (Kieser et al. 2015). ^{14}C data are reported as fraction modern carbon ($F^{14}C$), calculated according to Reimer et al. (2004) as the ratio of the sample $^{14}C/^{12}C$ ratio to the standard $^{14}C/^{12}C$ ratio (Ox-II). The $^{14}C/^{12}C$ ratios of the samples are background corrected (using the corresponding process blank) and the results of both the samples and standards are corrected for spectrometer and preparation fractionation using the AMS-measured $^{13}C/^{12}C$ ratio and normalized to the $\delta^{13}C$ (PDB) of –25‰. ^{14}C ages are calculated as $-8033\ln(F^{14}C)$ and reported in ^{14}C yr BP (BP = AD 1950) as described by Stuiver and Polach (1977). For regular sized samples between 0.7–1.5 mgC, the typical measurement precision reported is <= 3‰ for modern samples. To define limits of detection, if the sample measures within 2σ of the average process blank performance for that material type of the same size (which includes blank contribution from sample processing and measurement), we define this as a "non-finite" or "greater-than" measurement and the results are reported as such. For additional information regarding sample processing at AEL-AMS, see Crann et al. (2017).

RESULTS AND DISCUSSION

Table 1 summarizes the reference materials used for each material code, including process blank, secondary and modern reference materials. DIC/DOC reference materials are freshly prepared for each batch, where solid materials are dissolved in 20 mL of MilliQ water to yield 1 mgC (ideal), or size-matched to the samples processed alongside. Excellent yields (>95%, calculated from calibrated volume on multipurpose line) are obtained for all sample types. Procedural blank contributions are on the order of 5–7 µg modern carbon for DIC and DOC, and <1 µg modern carbon for CX and CH_4. Average performance of each standard is quoted in Table 1.

Performance of all process blanks for typical sized samples (0.7–1.5 mgC) are illustrated in Figure 2. During this 2-yr period, 34 DIC ($NaHCO_3$) and 53 DOC (kHP) standards were analyzed. The slightly elevated DIC blank samples (>1 pMC; 03-2016 and 03-2017) are likely attributable to atmospheric adsorption of CO_2 on the stock of $NaHCO_3$, despite being stored in a desiccant cabinet. Heating the powder in a 60ºC drying oven for 1 hr prior to use helps to reduce the blank. For DOC samples, a clear reduction of the blank is observed in early 2017 when a new stock of sodium persulfate was opened (same catalogue number, different lot number). Blanks are consistently reduced thereafter; demonstrating the importance of verifying the purity of each chemical lot. With the new stock of
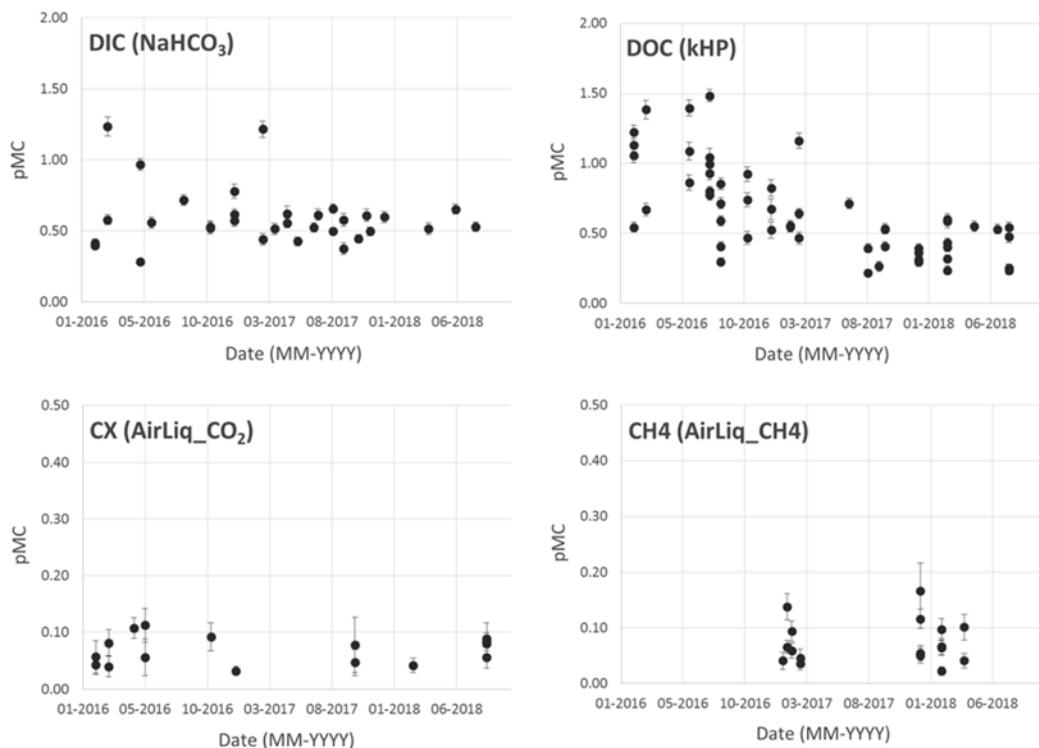
Figure 2   Process blank performance of water and gas samples at AEL by material code for standard sample sizes (0.7–1.5 mgC).

persulfate, process blanks are now consistently <0.7 pMC (>40,000 ^{14}C yr BP) for water samples, averaging around 0.55 and 0.44 pMC for DIC and DOC, respectively. This value is comparable to other DOC extraction methods such as UV oxidation (∼0.7 pMC blank; Druffel et al. 2013), and somewhat improved compared to other previously cited references including wet oxidation and evaporation (∼1.0 pMC blank: Burr et al. 2001; Leonard et al. 2013). We attribute the variability of the blank for both DIC and DOC to be related to modern carbon contamination during sample processing, from the bottles/septa, reagents, and He-carrier flow through line. Tests with varying amounts of MilliQ (10–100 mL) and AgNO$_3$ (1–10 mL) showed no significant change to the DOC blank. As expected, the relative contribution of the blank is elevated for smaller sized samples, illustrated in Figure 3. At ∼0.2 mgC, the blank is ∼3.6 pMC for DOC and ∼1.7 pMC for DIC; this indicates that the majority of the carbon contamination is contributed from the persulfate oxidation.

For secondary references, an average value of 41.06 ± 0.25 pMC was obtained from 30 analyses of IAEA-C2 (DIC), which agrees well with the consensus value. 4 SWRNOM and 6 OXII (DOC) secondary standards were run with average values of 106.12 ± 0.32 and 132.61 ± 0.45 pMC, respectively. The slightly depleted OXII value may be attributable to the fact that oxalic acid oxidizes very easily (Brett Walker, personal communication), and may have been pre-oxidized during the DIC sparge.
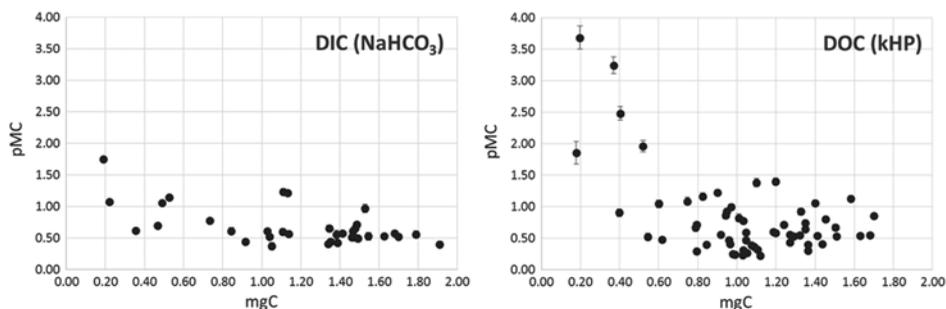
Figure 3   Blank contribution relative to sample size for waters (DIC and DOC).

A total of 16 CX and 17 CH_4 blank standards (^{14}C-free gas mixtures) were analyzed, all returning exceptionally low blanks, with values typically <0.1 pMC (>55,000 ^{14}C yr BP) and varying less than 0.2 pMC. The CX and CH_4 standards are more reproducible than the DIC and DOC materials as less sample preparation and handling is involved. Secondary reference materials for gas samples are not available at this time.

Highlights of the sample preparation method for waters include relative ease of preparation and high throughput. For DIC, typically 3–4 samples and 2 standards can be prepared and extracted in one day. DOC samples are slightly more labor intensive requiring a 2-day sample prep process since it is necessary to remove the DIC fraction prior to oxidation. Tests were completed leaving the reacted bottles 1, 3, and 7 days following heating, with no change observed with respect to sample yield or blank contribution, owing to the integrity of the butyl septa. Therefore, many samples (up to 20) can be prepared at once and left for up to 1 week until extracted, facilitating sample preparation. For gas samples (CX/CH_4) where there is minimal preparation required, typical throughput is ~8 samples per day. The wet chemical oxidation technique for DOC described in this paper has some disadvantages, namely that it can only be applied for non-saline waters as high concentrations of dissolved chloride will interfere with the persulfate oxidation. For ^{13}C stable isotope IRMS analysis, using the wet oxidation technique, the present routine limit for salt content is 1.5% (brackish water), which is considerably less than seawater (3.5%). So far, this limit has not been tested for the ^{14}C sample preparation. Small concentration samples (<1 ppmC) also prove challenging due to the large volume of water needed and limited reaction bottle size (max. 700 mL sample volume in 1000 mL bottle); however, multiple aliquots can be combined for a larger sample yield.

CONCLUSION AND FUTURE WORK

New techniques for preparation of water (DIC/DOC) and gas (CO_2/CH_4) samples for ^{14}C analysis at AEL-AMS highlight wet oxidation for dissolved organic carbon in freshwaters. Samples are prepared with relative ease and reasonably high throughput for a manual technique (5–8 per day) as many samples can be prepared at once prior to extraction. Measurement of reference materials demonstrate our ability to process water and gas samples with low procedural blanks: <0.7 pMC (>40,000 ^{14}C yr) for DIC/DOC, and <0.1 pMC (>55,000 ^{14}C yr) for CH_4/CX. Work underway to improve sample processing of waters and gases at AEL-AMS includes a number of manual and automated method development projects:

- Modification of the gas extraction line to accommodate larger volumes for ppm concentration gas mixtures (including atmospheric CO_2 and CH_4).
- Interface a robotic auto-sampler with a semi-automated gas cleanup line (St. Jean et al. 2017) for rapid analysis of carbonates, CO_2 in gas mixtures and waters (DIC and DOC).
- Adapt the wet oxidation method for DOC for brackish waters.
- Design and build a semi-automated, multi-capacity low-background UV-oxidation system for saline and low DOC concentration water samples.

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