METHOD: Combustion of organic carbon samples
EFFECTIVE DATE: 2/2/2023
APPROVED BY: Dr. Roberta Hansman

PURPOSE: To convert organic carbon to CO_2 by combustion in preparation for subsequent reduction to solid carbon and radiocarbon analysis.

INTRODUCTION: Organic carbon samples are converted to CO_2 either by combusting the sample in an Elemental Analyzer (EA) or in a quartz tube in the presence of copper oxide and silver (i.e., Closed-Tube Combustion or CTC). The method is chosen based on several factors including sample size and composition. For example, low %OC sediments and some samples with complex carbon components are combusted via CTC and not on the EA to preclude any potential carryover problems due to incomplete combustion.

For Elemental Analyzer (EA) combustion, the sample is weighed into commercially available tin cups, loaded into a carousel, and then an automated program proceeds. First the atmospheric gases are purged away with a continuous flow of helium. The sample is then dropped into a high-temperature furnace and rapidly combusted in the presence of pure oxygen. The tin is important to achieve a flash combustion at around 1800 °C. Resulting gases are carried by He over a chromium oxide combustion catalyst, then silver to remove sulfur and halides, and pure copper to remove any remaining oxygen. CO_2 is separated by gas chromatography and cryogenically trapped and then transferred to a glass manifold and moved to a graphite vacuum system for reduction to solid carbon.

For Closed-Tube Combustion (CTC) samples are weighed into pre-baked silver cups and combusted in a quartz tube in the presence of copper oxide, which supplies oxygen in excess for complete conversion to CO_2. The silver aids by scrubbing potential halides (e.g., chlorine) and sulfur, which can be trapped along with the CO_2 and poison the subsequent reduction reaction. The tube with sample and reagents is flame-sealed, placed in a furnace, and combusted at 900 °C for 3 hours. The samples are then placed in a tube cracker on the vacuum line, evacuated, cracked and the gas passed through an isopropanol and dry ice trap to remove water. The CO_2 is cryogenically trapped in liquid nitrogen, purified by pumping away non-condensable gases, quantified manometrically and transferred directly to a graphite reactor for reduction to solid carbon.

MATERIALS & APPARATUS

- Nitrile gloves, weigh paper and clean utensils (spatula, forceps etc.)
- Microbalance to weigh samples
- Liquid nitrogen and dewars
- Isopropanol and dry ice slush

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For EA:

- Elemental Analyzer and operating system
- Elemental Analyzer vacuum line with glass sample manifold and vacutap closures
- Ultra-high purity helium
- Ultra-high purity oxygen
- Tin capsules (5 x 9 mm, such as #041077 from Costech)

For CTC:

- Quartz combustion tubes (9 mm OD x 7 mm ID or 12 mm OD x 10 mm ID x 8" H; pre-baked at 900 ˚C)
- Copper oxide (pre-baked at 900 ˚C)
- Silver cups (5 x 9 mm; pre-baked at 550 ˚C for 3 h)
- Quartz tube inserts (various lengths and 6 mm OD)
- Vacuum pump out line with Ultra-Torr fittings

PROCEDURE:

For all combustion methods, samples are routinely prepared in groups of 10 that include 7-8 unknown samples, 1 process standard (approximately the size of the largest unknown), 1 process blank (1 mg C; KHP). If there are only 7 unknown samples, then 1 secondary standard (1 mg C) or 1 small mass standard or blank is included with the batch.

Wear gloves and use only clean utensils to handle and weigh samples.

Combustion by Elemental Analyzer (EA):

Weigh the sample into a tin capsule (typically 5 x 9 mm) using a microbalance. Transfer enough of the sample to produce ~1 mg of carbon (if possible). Record weight. Fold over the top to close the tin capsule with forceps then place it in a named cell in a culture tray. Record the position in the cell tray.

Prepare EA and adjoining vacuum line for CO_2 collection and storage. Turn on the carrier (UHP He) and oxidation (UHP O_2) gases; adjust flow rates according to EA specifications.

Fill dewars at the collection loops and vacuum line foretrap with liquid nitrogen. Place cryogenic water trap (isopropanol and dry ice slush) on EA vacuum line.

Re-zero any gauges (such as the baratron for pressure reading). Install and leak check glass sample collection manifold with vacutaps.

Place sample tin capsules in EA carousel. Operate EA program via operating system or software.

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Samples are burned and collected one at a time on the EA. The resulting CO_2 gas is cryogenically separated from the He carrier gas stream, and the CO_2 is quantified manometrically.

Samples are stored in individual storage ports on the glass sample manifold with vacutaps.

Closed-Tube Combustion (CTC):

Prepare tubes: weigh 250 mg CuO into 9 mm quartz tube. Combust assembled tube and any inserts required at 900 ˚C for 3 h.

Take care to never touch the sample or any part of the tubes that will be sealed with the sample.

If the sample is a sediment or powdery material, weigh the sample into a quartz insert tube and gently slide it into the prepared combustion tube. Alternatively, weigh the sample into a pre-baked Ag cup using a microbalance. Close up the cup with forceps and record the weight. Drop the sample into a pre-combusted and labeled CTC tube.

Attach combustion tubes with samples to a vacuum line, via the proper sized Ultra-Torr fitting, and gently pump down to a vacuum (< 5 mTorr).

Leak check the combustion tubes to ensure the samples will not have atmosphere mixed in them. Fix any leaks before proceeding.

Flame seal the combustion tubes 2 cm below the Ultra-Torr fitting.

Place sealed combustion tubes with samples into muffle furnace. Combust at 900 ˚C for 3 h to generate CO_2 from the sample.

RECORDS: Information specific to the processing of each sample is recorded in a notebook and in the NOSAMS relational database including operator, unique receipt number, mass, combustion method, and comments.