NOSAMS Facility

METHOD: Graphitization: Sealed Tube Zinc Reduction of CO_2 to solid C
EFFECTIVE DATE: 2/28/2024
APPROVED BY: Dr. Roberta Hansman

PURPOSE: To reduce pure carbon dioxide to filamentous carbon on an iron catalyst in a single tube with reagents for subsequent analysis in a sputter source AMS (Accelerator Mass Spectrometer). The process is depicted in the following reactions:

$$TiH_2 + \text{heat} \xrightarrow{440\,^\circ C} 2H_2 + Ti$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$

$$CO_2 + Zn \rightarrow CO + ZnO$$

$$CO + H_2 + Fe \xrightarrow{500^\circ C\ (3\ hr) - 550\,^\circ C\ (4\ hr)} C_{graphite} + H_2O$$

INTRODUCTION: The sealed tube zinc reduction method (Xu et al 2007) is used in addition to a hydrogen reduction method at NOSAMS to produce graphite for samples > 500 µg C. Both methods catalytically reduce CO_2 to solid carbon on 2.5 mg iron and achieve a precision of 2-3‰ with analogous low backgrounds for samples in this size range. The reaction takes 5 hours to complete. Sample batches are normally produced in batches of 10 with control samples embedded. When requested, a split of CO_2 is saved prior to reduction for IRMS $\delta^{13}C$ analysis.

The NOSAMS Sample Preparation Lab vacuum lines are designed to introduce CO_2 gas efficiently from 10-port manifolds, but gas may also be introduced via single ports. Once the vacuum line is set up and leak-checked, each sample is manually introduced then transferred through a water trap to a known volume for manometric determination of mass. If required, the sample is split into an appropriate size and a split taken for $\delta^{13}C$ analysis. The sample is then transferred to a tube preloaded with reagents, flame-sealed and placed in a muffle furnace for a programmed bake at 500° C for 3 hours and 550 °C for 4 hours.

MATERIALS & APPARATUS

- Fe powder, reduced 98%, Mallinckrodt -325 mesh
- Zinc powder 100 mesh 99.995% (Aldrich #324930)
- Titanium(II) hydride, 99% (Thermo Scientific Cat. No. 012857-06)
- Pre-baked 6 mm OD × 50 mm borosilicate tubes (DWK Life Sciences 73500650)
- Pre-baked 9 mm OD ×180 mm borosilicate tubes
- Liquid Nitrogen and dewars
- Vacuum system, including manometer
- Flame-sealing torch
- Programmable temperature combustion oven

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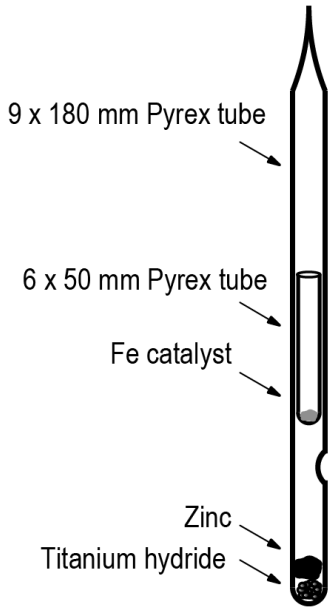
PROCEDURE:

Preparation of graphite reduction tubes:

Using a torch, create a dimple in the 9 mm OD tube for the inner 6 mm tube to rest upon. Bake all tubes for 2 hours at 550 °C to remove contaminants prior to use. Add 10-15 mg TiH_2 to the bottom of a pre-baked 9 mm OD tube as shown in the figure below using a cleaned, dedicated stainless steel funnel. Dispense 30–35 mg Zn powder into the bottom of the same tube using a second dedicated funnel. Do not touch the inner tube containing catalyst with your hands. Using gloved hands and tweezers, dispense 2.5 ± 0.15 mg iron catalyst that has been conditioned by baking at 450 °C under 1.2 atm of hydrogen into the bottom of the 6 mm tube. Use tweezers to slide the smaller tube with catalyst into the larger tube to rest on the dimple. Bake the assembled tubes for one hour at 300 °C and store in a desiccator for up to two weeks.



Prepare a slush water trap in a dewar with isopropanol alcohol and dry ice and place it on the water trap. Fill a 2- or 4-liter liquid nitrogen dewar for use in cryogenically transferring CO_2. Place prepared graphite tubes onto the vacuum line and tighten Ultra-Torr fittings to seal. Evacuate the tubes slowly and pump for 20 minutes. Leak check the line. Zero the pressure transducer. Introduce a CO_2 sample and transfer it cryogenically to the baratron region for manometric quantification after passing through a water trap to ensure complete removal of water. Pump away non-condensable gases (if present) by pumping over the

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frozen CO_2. Lower the LN_2 trap then isolate and allow the CO_2 to expand into the calibrated volume. Take a pressure and temperature reading to determine sample mass (values saved to the database). If necessary, split the sample using calibrated known volumes and transfer the CO_2 to a graphite reactor. Flame-seal the CO_2 into the graphite tube and place it in a rack. Repeat this sequence for all samples in the batch. When cooled, place the tubes in a programmable temperature oven and set for 500 °C for 3 hours and 550 °C for 4 hours. Graphite can be stored vacuum-sealed in these tubes indefinitely until ready to be cracked and pressed into cathodes for AMS analysis.

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, method, and comments.

REFERENCES:

Xu X, Trumbore SE, Zheng S, Southon JR, McDuffee KE, Luttgen M, and Liu JC. 2007. Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing background and attaining high precision. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms Accelerator Mass Spectrometry- Proceedings of the Tenth International Conference on Accelerator Mass Spectrometry 259:320-329; DOI: 10.1016/j.nimb.2007.01.175