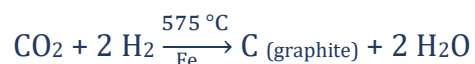


# NOSAMS Facility

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METHOD: Graphitization: Hydrogen reduction of CO<sub>2</sub> to solid C  
EFFECTIVE DATE: 2/1/2023  
APPROVED BY: Dr. Roberta Hansman

**PURPOSE:** To reduce pure carbon dioxide to filamentous carbon (graphite) on an iron catalyst for subsequent analysis in a sputter source AMS (Accelerator Mass Spectrometry) system. The process is depicted in the following reaction:



**INTRODUCTION:** A modified Vogel reduction method (Vogel et al. 1984) is used at NOSAMS to produce graphite with pure hydrogen gas and iron to catalytically reduce CO<sub>2</sub> to solid carbon. Individual ovens are placed over reaction tubes and the CO<sub>2</sub> is reduced at 575 °C to filamentous graphite on the Fe catalyst in the presence of hydrogen. A second tube containing magnesium perchlorate traps any water produced as a by-product. The reaction typically averages 2-3 hours to complete. Pressure and temperature are automatically collected for each reactor to assure completion and to calculate manometric yield. Sample batches are normally produced in batches of 10 with control samples embedded. When requested, a split of CO<sub>2</sub> is automatically saved prior to reduction for δ<sup>13</sup>C analysis by IRMS.

The NOSAMS Sample Preparation Lab vacuum lines are designed to introduce CO<sub>2</sub> gas efficiently from 10-port manifolds, but gas may also be introduced via single ports. Once the line is set up and leak-checked, a custom program controls sequential gas transfers, records the sample mass, takes a split of CO<sub>2</sub> and transfers it to a manifold for IRMS δ<sup>13</sup>C analysis, then records pressure and temperature as the reactions progress. Applications display the system state in a graphical diagram and provides automatic or direct, manual control.

NOSAMS has several semi-automated graphite lines controlled with National Instruments controller cards and LabView routines. For these, air pressure is used to open and close Vacutap™ valves programmatically. In 2021 NOSAMS acquired and installed a customized Carbon Extraction and Graphitization System (CEGS) from Aeon Laboratories, L.L.C. (Goehring et al. 2019) specifically adapted for our 10-port manifold system. All systems complete the same tasks to control the reduction process.

## MATERIALS & APPARATUS

- Mallinckrodt Fe powder, reduced 98%, -325 mesh
- High purity hydrogen gas
- Argon gas
- Pyrex graphite reactor tubes 50 mm H x 6 mm OD (Fisher # 14-957AA)
- Liquid Nitrogen and dewars

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- Vacuum system, including manometer and ovens
- Magnesium perchlorate

*Note: All Pyrex glassware is pre-baked at 575 °C for 1 h prior to use.*

## **PROCEDURE:**

### ***Prepare and dispense Fe powder***

Fe catalyst is prepared for dispensing by treating several grams under vacuum in a 9 mm OD tube. The tube is backfilled with 1.2 atmospheres of hydrogen gas, an oven is placed over the tube and the catalyst is heated for 1 hour at 450 °C. Once cool, the tube is capped and stored in a desiccator for up to three weeks.

Graphite reactor tubes are prepared by dispensing  $2.5 \pm 0.15$  mg of prepared Fe catalyst into the bottom of 50 mm H x 6 mm OD glass tubes. The same amount of catalyst is used for all sample masses analyzed by AMS.

### ***Prepare and run automated graphite line***

Place reactor tubes with Fe catalyst onto the vacuum line in the horizontal position and tighten the Ultra-Torr fittings to seal. Prepare tubes containing ~5 mg magnesium perchlorate into 50 mm H x 6 mm OD tubes and place them below the tubes with Fe in the vertical position for use as a water trap for each reactor. New perchlorate is used each time.

Check that all valves are properly greased and open and close properly. Evacuate the reactors slowly at first using the needle valve, and pump fully for 20 minutes. Leak check the reactors and the transfer lines.

Turn the ovens on but wait until heated to place them over the tubes with catalyst. Condition the catalyst by baking for 15 minutes at 575 °C under vacuum. Remove ovens while continuing setup.

Prepare a slush water trap with isopropanol alcohol and dry ice for use in the baratron region and fill large liquid nitrogen dewars for use during the automated run.

Zero each pressure transducer. Open all large dewars for automated LN2 supply. Enter all sample identification information into the program. Open valves for hydrogen supply and purge if necessary.

### ***Automated run:***

During the automated run, CO<sub>2</sub> is initially transferred cryogenically to the baratron region for manometric quantification after passing through a water trap to ensure complete removal of water. Non-condensable gases (if present) are pumped away by pumping over the frozen CO<sub>2</sub>. The LN2 trap is

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lowered, the CO<sub>2</sub> is then allowed to expand into a calibrated volume and a pressure reading is taken to determine sample mass (values saved to the database). The sample is then transferred cryogenically to a graphite reactor and valves closed to isolate the sample reactor from the line. This sequence is repeated for all samples in the batch.

Once all samples are loaded into reactors and the program is paused, ovens are placed back on the reactors and logging of pressure and temperature begins.

When reduction is complete, the ovens are removed, and the line is backfilled with argon. Tubes with graphite are removed, capped, and labeled with bar-coded stickers displaying the graphite number. Graphite is stored in a desiccator for AMS analysis.

*Note: This procedure is in use for sample sizes down to approximately 25 µg C. For small and ultra-small graphite production methods, see Pearson et al. 1998 and Shah Walter et al. 2015.*

**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.

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