NEC-Aeon Carbon Extraction & Graphitization System

National Electrostatics Corp.

Carbon Extraction & Graphitization System (CEGS)

The CEGS is a laboratory instrument designed to process samples for Accelerator Mass Spectrometry (AMS). Various models are available, to provide general-purpose or specialized service and to balance system cost with the technical and logistical requirements of the laboratory receiving it.

Each CEGS features fully automated process control, with stepped combustion, CO_2 collection, purification, measurement, and reduction to graphite integrated into a single, seamless process.

The operator loads pretreated samples into the configurable inlet ports and enters the sample data into the system computer, selecting the desired process for each sample. Once the "Start" button is clicked, the system automatically executes the selected process for each sample in sequence and notifies the operator by email when the run is complete.

Each system is capable of processing a full suite of organic samples in a 24-hour period. Throughput for digested carbonates and gas samples can be higher, potentially up to 24 per day, depending on sample sizes, process selection, and operator availability.

Carbon Content Measurements

A brief synopsis of the AMS process provides a useful context for clearer understanding of how the CEGS fits in. The sample undergoes a series of functional phases before measurements.

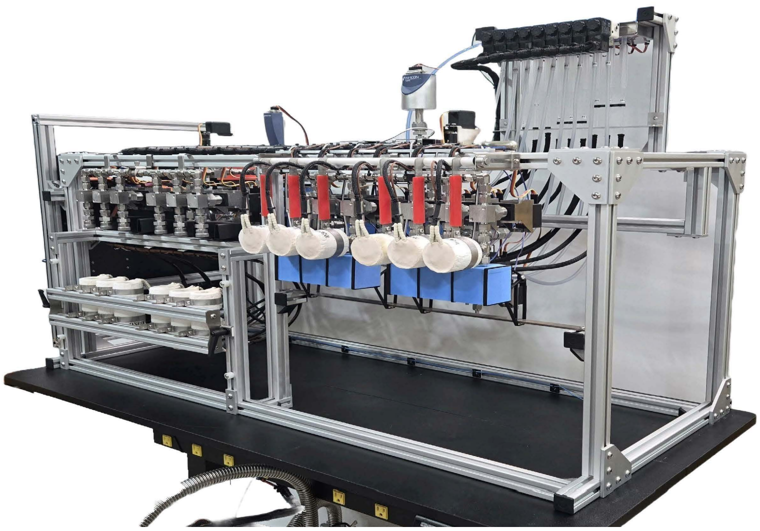
Pretreatment

First, a representative fraction of the submitted material is isolated for further processing. Any carbon-bearing matter that might be older or younger than the target fraction must be removed. Often, specific carbon compounds are selected by employing chemical reagents to separate them from the other substances present. Additionally, steps may be taken to remove or avoid the formation of non-carbonaceous chemicals that might interfere with subsequent steps. This phase is sometimes called "wet chemistry".

Extraction

After pretreatment, the sample's carbon must be separated from the rest of the sample material. To obtain an accurate analysis, all non-sample carbon, such as CO_2 from the air, must be excluded. A vacuum system is usually employed to remove air, and carbon-free gases such as research-grade oxygen, helium, argon, or nitrogen are introduced to participate in the extraction. The collected carbon must come exclusively from the sample material. Moreover, all of the the sample's carbon must be collected. Due to fractionation effects, an incomplete or partial carbon extraction can compromise the result as well. The technique for liberating the carbon from pretreated material varies based on the type of sample, but most commonly it is either combusted (burned) or digested in acid.

In either case, oxygen combines with the carbon to form carbon dioxide (CO_2). Other chemical reactions usually take place simultaneously, so steps are taken to remove unwanted reaction products, such as water, sulfur and halogen compounds, nitrogen oxides, and so on. To summarize in simple terms, extraction consists of carbon liberation, CO_2 collection, and purification.



CEGS LL6 Model

CEGS 12X Model

Graphitization

This phase uses hydrogen to remove the oxygen from the purified CO_2, leaving behind solid carbon. The carbon is deposited onto powdered iron, which serves as a catalyst for the reduction and a substrate for the deposition. The solid carbon is commonly called "graphite", although this term is not strictly correct, because it doesn't have a layered graphene structure.

Isotope Analysis

Finally, the "graphite" is compressed into a tiny, cylindrical aluminum "cathode" or "target" and inserted into the ion source of an accelerator mass spectrometer. Ionized cesium is sputtered onto the graphite's surface, which ionizes the carbon atoms. Electric fields focus and accelerate the charged atoms through a strong magnet which deflects them toward a set of particle detectors. The lightest atoms (^{12}C) are deflected more than the heaviest ones (^{14}C), so they can be separated for measurements. The ratio of ^{14}C atoms to ^{12}C in the sample is then used to determine the ratio of modern carbon to fossilized carbon.

The Role of the CEGS

The CEGS is computer-controlled machine that automatically performs the middle part of the processing of AMS samples. These tasks traditionally were performed by a researcher using a separate specialized manual vacuum apparatus for each step. They fell collectively under a broader definition of *Pretreatment* that includes everything before *Isotope Analysis.*

Combining extraction, purification and graphitization into a single instrument eliminates sample transfers, which are a source of contamination. Automation significantly reduces sample loss due to human error, and ensures extremely consistent temperatures, pressures, and process step times. An important consequence of this is reduced scatter in the analytical data, which leads to better statistics, lower uncertainties, and more reliable ratios.

Configuration Options

Each CEGS contains graphite reactors and inlet ports, with a Process Section in between.

Graphite Reactors

The reduction from CO_2 to 'graphite' typically takes about two hours, but can require anywhere from 30 minutes to three hours, depending on the amount of carbon in the sample. For practical purposes, the number of reactors governs the throughput of the system (how many samples can be processed in a day), and this is the first figure in the CEGS model number. Throughput can also be influenced by managing the purification process and controlling sample size. Both of these may be accomplished by adjusting the instrument settings.

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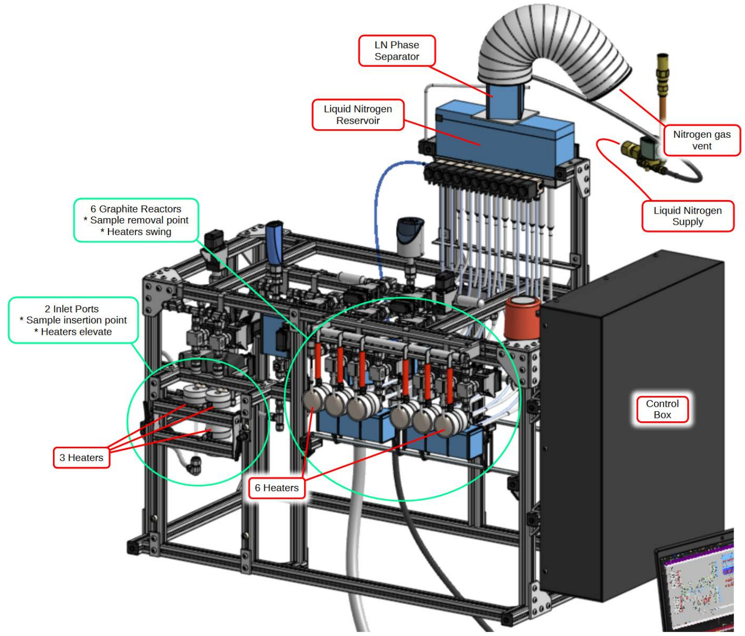
The Low-Level Options

An important configuration option is the selection valves in the sample path through the CEGS.

In a standard CEGS, plug valves are used throughout the system, owing to their high-conductance, low cost, and ease of operation. Plug valves contain elastomeric (O-ring) seals, which have a non-zero permeability to gases, including carbon dioxide. The total amount of CO_2 that can diffuse through all of the seals in the CEGS while a sample is in process is very tiny, on the order of 0.01 µmol. The contamination potential from permeation is even lower than this figure suggests, though, because for most of the process time, the sample is in contact with very few seals, and gases permeating through the rest of the sample path are pumped away. This means that for most samples, the contamination potential from elastomeric seals is sufficiently far below the activity measurement uncertainties as to be negligible.

However, "low-level" samples have extremely small amounts of radiocarbon. These samples are very old (> 35,000 years), or very small (< 2.5 µmol, or 30 µg C), or they are both. Especially in the last case, the contamination potential from elastomeric seal permeation may become significant. By replacing the valves in the sample path with ones that use only metal seals, this potential source of error can be practically eliminated. Unfortunately, metal-sealed valves have a lower conductance and much longer actuation times. Additionally, they cost significantly more and require more expensive actuators. Therefore, they are recommended only when the benefits outweigh the drawbacks.

The CEGS variants that feature all metal-sealed valves in the sample path have model numbers that begin with "LL", to signify their ability to quantitatively handle low-level samples.



LL6x1+1+VP Model

Inlet Ports

The number of inlet ports can be selected to meet the laboratory's needs. Most often, the number of inlet ports either matches the number of reactors or there is only one (X1). For example, a CEGS 6X system has six inlet ports (matching the number of reactors), while a CEGS 6X1 has six reactors and one inlet port. The X1 variants have the advantage of lower cost while achieving a similar throughput, with a slightly different workflow.

When the number if inlet ports equals the reactors, the daily workflow is:

1. Start of day: Remove yesterday's samples and load new reagents.
2. Load a batch of samples into inlet ports and start the sequence.
3. Wait for next day.

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When there is only one inlet port:

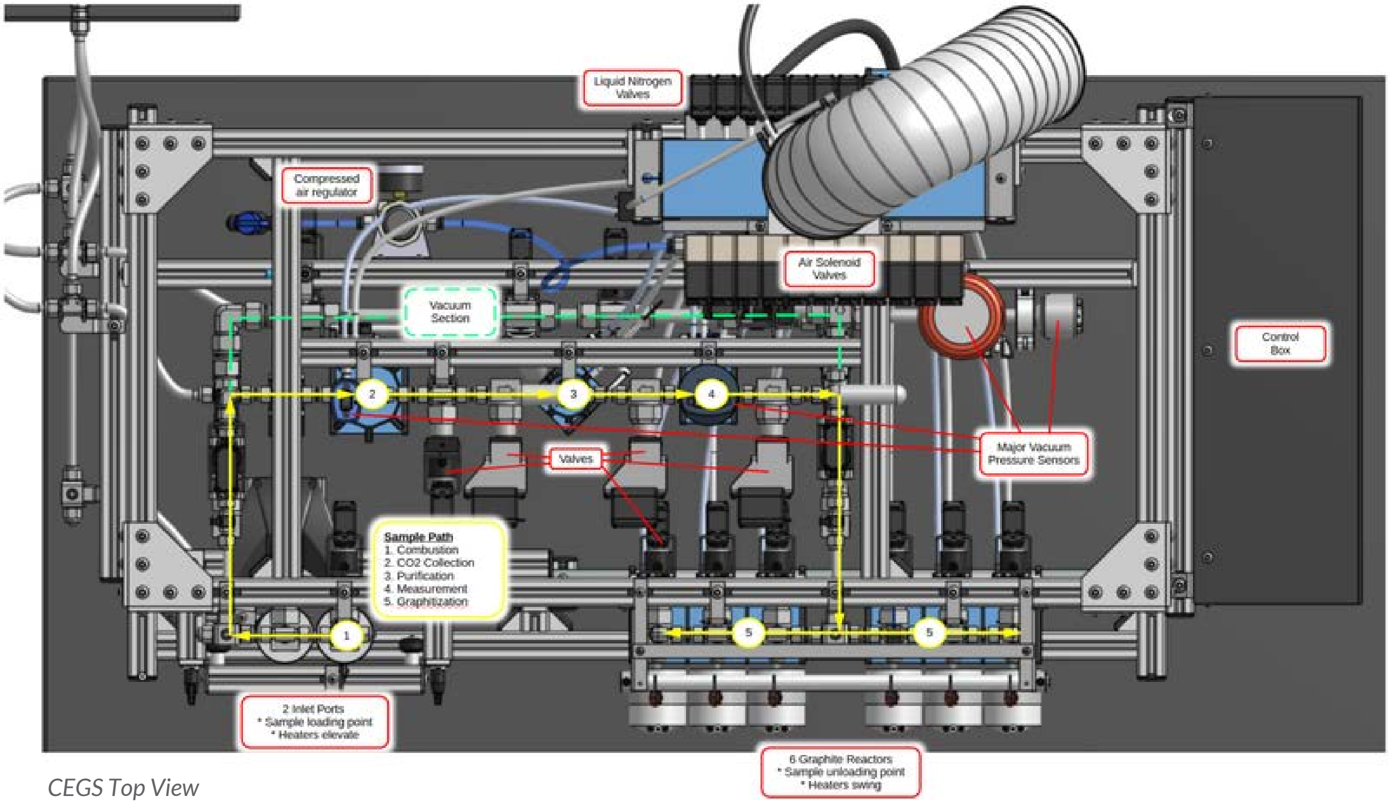
1. Start of day: Remove yesterday's samples and load new reagents.
2. Load the first sample into the inlet port and start it.
3. When the system notifies the operator, load the next sample and start it
    a. Repeat as needed as long as more samples and reactors are available.
4. Wait for next day.

If the lab has a modest throughput and someone is available to occasionally load a sample, an X1 can be a perfectly adequate solution. If lab staff is limited, or if full batches are produced regularly, the additional inlet ports are more convenient.

Other Configuration Options

For special applications (such as in situ cosmogenic radiocarbon dating, or ramped pyrolysis/oxidation), additional dedicated inlet ports are frequently included, and other devices may be added, such as tube furnaces, tandem coil traps, and CO_2 analyzers.

Where CO_2 splits for independent stable isotope ($\delta^{13}C$) analysis are required, the CEGS is fitted with a supplementary outlet manifold of gas ports. The gas split ports may be of two types. One has a fitting to accept a 6 mm pyrex tube to collect the split in a flame-sealable ampule ("ampule port"). The other type ("vial port") has a needle to pierce into a septum-sealed vial commonly used on IRMS gas bench autosamplers. With vial ports, the CEGS can automatically post-fill the vial to slightly over atmospheric pressure with inert gas (He or N2, not Ar) to facilitate processing at the IRMS lab.



CEGS Top View

Carbon Extraction & Graphitization System (CEGS)

Specifications

✓ Fully automated sample process control

✓ Accepts organic, carbonate, and gas samples

✓ Wide sample mass range
- *Standard systems:* 30 µg to 2.7 mg C
- *Low-level systems:* 5 µg to 2.7 mg

✓ Online, stepped-temperature combustion is built-in and user-definable
- Recommended step temperature range: 150 to 850 °C
- Up to 1100 °C is possible but lower temperatures prolong furnace element life

✓ Quantitative sample CO_2 capture and purification
- High-vacuum: < $1e^{-4}$ Torr ultimate pressure guaranteed, < $2e^{-5}$ typical
- Liquid nitrogen trapping and cooling
- Special trace sulfur trapping capability for samples with problematic sulfur content

✓ Precision, calibrated variable temperature cold finger for cryogenic purification
- Temperature range: -180 to +50 °C
- Absolute precision: ± 5 °C
- Repeatability: < 1 °C
- Stability: ± 2.0 °C

✓ Accurate CO_2 measurement
- 2 to 3000 µg C: ± 1 % of reading or 1 µg C
- 0.17 to 250 µmol: ± 1 % of reading or 0.08 µmol

✓ Configurable small sample processing
- Small samples can be graphitized directly, like larger samples, or diluted with ^{14}C-free CO_2 to a configurable minimum graphite mass
- Dilution may be disabled or enabled automatically based on the amount of carbon in the sample

✓ Minimal sample cross-contamination, blanks and modern samples can be run back-to-back

✓ Optimal graphitization conditions
- Precise process gas quantities and pressures for excellent H2:CO_2 ratio control
- Accurate, tuned PID furnace temperature control
  - Absolute temperature precision: ± 10 °C
  - Repeatability: < 2 °C
  - Stability: ± 3 °C
- Small graphite reactor volume: ~3 mL
- Graphite reduction completion is automatically checked by residual pressure

✓ Very low process blank levels, typically < 0.002 fM*
- *Achievable, i.e., not limited by CEGS; remains dependent on lab practice and AMSperformance.
- Typical "empty" blank level < 0.2 µg C

✓ Low manpower requirements: typically less than 5 minutes per sample

✓ Very little inter-sample equipment maintenance (normally zero)

✓ Minimal routine maintenance

✓ Continuous recording of all important sample, process, and equipment conditions
- Sample combustion, collection and extraction conditions
- Graphitization temperature and pressure profiles

✓ Free Data Visualizer tool graphs logged data in real-time

- Daily archives are available for viewing at any time, even years later

✓ The control system software is fully customizable and comes pre-configured for your CEGS
- Sample processes can be easily defined and updated with the intuitive, built-in point-and-click editor.
- The delivered initial configuration includes common process sequences appropriate for most sample types.

Contact NEC

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