

## **Standard Operating Procedure**

### **Dissolved Gas Analysis (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) on SRI Gas Chromatograph with Bandelero Auto-Sampler V 1.0**

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## **I. Purpose and Scope**

This procedure describes the methods used for analysis of dissolved gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) from headspace equilibration samples using an SRI gas chromatograph (GC) equipped with a Bandelero auto-sampler. It includes instrument setup, calibration, sample analysis, data processing, quality assurance/quality control (QA/QC), and NEON data reporting.

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## **II. Principle**

The GC separates gaseous analytes via packed columns. Following separation, detection is performed by:

- Flame Ionization Detector (FID) with methanizer for CH<sub>4</sub> and CO<sub>2</sub>.
- Electron Capture Detector (ECD) for N<sub>2</sub>O.

Detector responses (peak areas) are compared to standard curves from certified calibration gases to quantify unknown concentrations.

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## **III. Equipment and Materials**

- SRI GC with FID, methanizer, and ECD
  - Bandelero auto-sampler
  - Carrier gas: Ultra High Purity (UHP) nitrogen (N<sub>2</sub>)
  - FID fuel: hydrogen (H<sub>2</sub>; supplied by paired 2022-H100 hydrogen generator)
  - Certified gas standards (e.g., Airgas certified gas standards)
  - 20-ml luer lock plastic syringes
  - 0.6mm x 25mm needles (23 gauge)
  - Three-way stopcocks
  - Evacuated 12 mL Exetainer vials
  - Windows computer with PeakSimple software
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## **IV. Calibration Standards**

1. Fill evacuated exetainers with calibration standards from certified gas standards. Vials will be filled with six calibration mixes (S1-S6). Each calibration standard is a mix of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O balanced with Ultra-High Purity Air.
    - a. Connect 20-ml luer lock plastic syringe with three-way stopcock and 23-gauge needle to regulator.
    - b. Flush needle and syringe at least three times.
    - c. Fill syringe with 20 mL of standard gas.
    - d. Working quickly, expel excess to exactly 15 mL; immediately pierce evacuated vial septum and inject full 15 mL. Maintain plunger pressure during vial removal.
  2. Prepare extra check standards (i.e., near ambient concentration standard; S2) using the same method as Step 1.
  3. Prepare method blanks using Ultra Zero Air and the same procedure.
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## V. Instrument Start-Up

1. Replace collector electrode.
  2. Open N<sub>2</sub> carrier gas; ensure cylinder pressure >500 psi; set regulator to 60 psi.
  3. Start hydrogen generator.
  4. Switch on GC main power.
  5. Launch PeakSimple software and confirm GC connection.
  6. After ~30 min, verify FID ignition (e.g., condensation in exhaust).
  7. Allow ≥12 hours warm-up prior to analysis.
  8. Make a copy of the sample table template and rename with “GC\_” plus the date of analysis (e.g., GC\_20251001). The template is set up with a typical positions for standards, check standards, and method blanks for a 60-sample run (e.g, rows 1-10 ambient air, rows 11-17 method blank + 6 calibration standards (S1-S6), rows 18-19 ambient air, rows 20-39 samples, rows 40-41 method blank and check standard (S2), rows 42-61 samples, rows 62-63 method blank and check standard, rows 64-83 samples, rows 84-85 ambient air, rows 86-92 method blank + 6 calibration standards (S1-S6).
  9. Load standards and samples into Bandelero; record samples into the template. Remove any extra rows and adjust the position of last suite of calibration standards to follow the last samples. Ensure that
    - A full suite of standards is loaded before and after the samples.
    - Method blanks and check standards are interspersed between every 20 samples.
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## VI. Instrument Run

1. Confirm “Ready” status via green indicator on GC front panel.
2. Start Bandelero vacuum pump.
3. Enable auto-sampler (“B” command).
4. Begin run with 10 ambient air samples (vials without septa) to verify low levels of baseline noise (< 30 μV), symmetrical, well-defined peaks, and expected retention times:

- CH<sub>4</sub>: 2.25–2.75 min (FID)
  - CO<sub>2</sub>: 4.310–4.810 min (FID)
  - N<sub>2</sub>O: 5.900–6.100 min (ECD)
5. If baseline noise, peak shapes, and retention times are acceptable, proceed with full batch: calibration standards, ambient air, samples (with blanks and check standards every 20 samples), ambient air, and final calibration standards.
  6. If baseline noise, peak shapes, and retention times are unacceptable, troubleshoot as described in Section X.
  7. Monitor GC hourly during run (needle position, gas pressures, baseline, peak shape and timing).
  8. Upon completion:
    - Power down GC.
    - Shut down hydrogen generator.
    - Close N<sub>2</sub> carrier gas.
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## VII. Calibration Verification

1. Analyst will review all chromatograms in 3D Imager for peak shape and proper integration.
  2. If acceptable, retrieve run data files from instrument log. Acceptable means that, visually, peak shapes are approximately symmetrical, and the auto-integration found the start and end of the peak.
  3. If unacceptable, troubleshoot as described in Section X, run calibration standards to ensure acceptable, re-run samples according to Section VI.
  4. Generate separate calibration curves for pre-sample and post-sample standards.
  5. Use the calibration curve from the pre-sample standards to calculate percent recovery for the post-sample standards as (calculated partial pressure – known partial pressure)/ known partial pressure. If the recovery of the post-sample standards that deviates more than 5% (for ambient and above concentrations), troubleshoot as described in Section X before continuing.
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## VIII. Data Processing and QA/QC

1. Analyst will export instrument data and merge with run-specific sample table (e.g., GC\_20251001) in R using existing code according to internal LMS ID.
2. Verify that two full suites of standards (one before the samples and one after the samples) and method blanks/check standards (interspersed between every 20 samples) were run and met requirements described in section VII. Calibration Verification.
3. Apply calibration curves to sample peak areas.
4. Calculate % deviation of a mid-range check standard (S2); must be  $\leq 5\%$ .
5. Flag for re-analysis:

- Samples exceeding calibration range. These samples can be diluted and re-run. Note this dilution in the per-sample data report.
  - Runs with check standard deviation > 5 %.
6. Prepare results for NEON submission.
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## IX. NEON Data Reporting

1. Submit per-sample CSV (Attachment 2c) including:
    - CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>O concentrations (ppmv)
    - Precision (CV%) from at least three check standards (calculated as standard deviation / mean of near-ambient standard values)
    - Certified standard accuracy (%) from the standard COA
  2. Submit batch QA CSV (Attachment 2d) with certified standard details.
  3. Submit lab summary CSV (Attachment 2e) annually and after major method changes:
    - Method Detection Limit (MDL):  $t\text{-value (99\%)} \times \text{standard deviation of } \geq 7$  replicate near-ambient standards (S2).
    - Uncertainty: Type A, calculated from replicate near-ambient standards and check standards.
    - Long-term precision (CV%) calculated as standard deviation / mean for all check standards run during the summary time period.
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## X. Troubleshooting

- No peaks: Check carrier/fuel gas pressures, FID ignition, and system for leaks.
- Poor peak shape or noisy baseline: Bake out columns; replace collector electrode.
- Retention time shift: Verify temperature setpoints and flow rates.
- After fixing issue (or if no issues found), run at least two full sets of calibration standards and assess for % recovery (described in Section VII 5)
- If no issues found, re-run samples.