Standard Operating Procedure
Chemiluminescence NO Analyzer - Eco Physics CLD 88Y

Chemiluminescence technique is the leading measurement method for detecting nitrogen oxides worldwide. The Eco Physics CLD 88 yet is a vacuum chemiluminescence NO analyzer with a digital display of the concentrations and diagnostic messages. This 800 series analyzer is modularly designed to allow the incorporation of the vacuum pump and thermal ozone scrubber inside the case of the analyzer. It has fast response time, unheated, ambient level chemiluminescence effect with a single reaction chamber. External restriction option (e) and shut off valve (t) provide for flexibility in sample flow rates.

1.0 Operation Procedure

Exhaust gas
- The vacuum pump exhaust must be allowed to vent either above roof level or to a special-purpose ventilation system using a tube with a minimum inner diameter of six millimeters. Neglecting to observe this safety precaution may cause severe health problems (e.g. the inhalation of NO₂ may cause irritation of the respiratory tract or in severe cases to lung damage.)

High pressure gas
- Pressurized gas cylinders must be secured against falling. Horizontally stored cylinders must be prevented from rolling.
- The pressure reduction valves and all tubing from gas cylinder to vent must be regularly checked for leak tightness.

Toxic gases
- Nitrogen monoxide (NO), especially Ozone (O₃) and nitrogen dioxide (NO₂) are toxic!
- Ozone – low concentrations of ozone can be harmful to the upper respiratory tract and the lungs. The severity of injury depends on both by concentration of ozone and the duration of exposure.
- NO₂ – nitrogen dioxide is toxic by inhalation. Symptoms of poisoning tend to appear several hours after inhalation a low but potential fatal dose. Low concentrations (4 ppm) will anesthetize the nose, thus creating a potential for overexposure.

Specific dangers with the NO Analyzer
- NO – Nitrogen monoxide is used only for calibration. This should be performed at a similar concentration as the expected concentration of the sample gas.

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• **NO₂** – For the determination of NO₂, the converter shall be checked by the principle of gas-phase-titration (GPT). However, when using bottled NO₂, extreme care shall be observed on account of the high toxicity to avoid any leakage of the gas.

• **O₃** – Ozone is produced inside the analyzer in the ozone generator using dried ambient air. In a correctly installed and operated system, this ozone will be destroyed in the ozone scrubber located on and immediately upstream of the vacuum pump. Furthermore, the actual concentration of ozone is low, and under fault conditions the ozone generator is automatically shut down by the analyzer control system.

1.1 Sample Pre-treatment

**CO₂ capture samples:**

a. Prepare 20 mL 40 g/L sulfamic acid solution: Weigh 0.8 g sulfamic acid and dissolve in 20 mL deionized water.

b. Prepare 20 ml 5x diluted sulfuric acid solution in deionized water from 98% concentrated sulfuric acid.

c. For CO₂ capture samples: Add 2 mL deionized water into amber vial. Then add 200 µL sample solution. After mixing well, inject 500 µL of the 40 g/L sulfamic acid solution and 150 µL of the 5x diluted sulfuric acid solution sequentially to destroy nitrite. Mix well and store in a dark place for 15 minutes. The total dilution for the sample is 14.25x.

**Environmental water samples:**

a. Prepare 5 mL 20 g/L mercuric chloride solution in deionized water. Stored in fridge. Good for two weeks.

b. Prepare 5 mL 50 g/L sulfanilamide solution in 1 N hydrochloric acid. Stored in fridge. Good for two weeks.

c. For environmental water samples (NOT CO₂ capture related): Add 40 µL mercuric chloride solution to the 0.74 mL final extract (organic solvent extract), mix well, and store in dark for 30 min. Then add 40 µL sulfanilamide solution, mix well, and store in dark for 15 min.

1.2 Connect Reaction System

a. Secure the reaction chamber onto the support stand with two clamps. Connect with heated water tubing as shown in the following picture. The heated water enters at the bottom and exits through the top.

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b. Clean reaction chamber
   ✓ Connect \( \text{N}_2 \) cylinder with gas inlet of reaction chamber.
   ✓ Turn on \( \text{N}_2 \) gas and rinse reaction chamber with DI, MeOH, DI, and then glacial acetic acid. Make sure there is gentle gas flow when there is liquid in the chamber.

c. Connect condenser
   ✓ Condenser: Attach the stand-alone condenser (i.e., no tubing connected to base trap) on top of reaction chamber. Clamp to secure (see the picture as above).
   ✓ Attach cooling water tubes to condenser: inlet at bottom and outlet at top.

d. Connect base trap
   ✓ Fill 100 mL 1 N NaOH into base trap. Change liquid weekly. Function: remove \( \text{NO}_2 \), capture acetic acid vapor escaped from reaction chamber.
   ✓ Use a little vacuum grease and clamp to prevent leak and reduce etching of glass by base solution.
   ✓ Place base trap in secondary container and then fill with ice-water mixture for cooling. Make sure there is solid ice throughout the run, as increasing temperature will lead to unstable background.
   ✓ Attach top of base trap to support stand with clamp to prevent disconnection from bottom of base trap.
   ✓ Connect gas tubing between top of condenser to base trap. After tubing is connected, the pressure reading should be close to zero.
1.3 System Warm-up
   a. Turn on CLD 88 Y et – switch on the back. It takes ~40 min to power up: PWUP shown on the top right-hand corner.
   b. Turn on 80 °C bath for reactor jacket. Check water level.
   c. Turn on cooling bath – set at slightly above 0 °C, final temperature stabilizes at ~ 4 °C (thermometer reading).

1.4 Triiodide solution preparation
   a. Prepare triiodide solution fresh before the analysis
      ✓ Weigh 2.16 g potassium iodide and 0.456 g iodine
      ✓ Dissolve in 4 mL deionized water
      ✓ Make sure all solids are dissolved in the triiodide solution (may be hard to see with the brown color).

1.5 Fill Reaction Chamber
   a. Add 15 mL glacial acetic acid to the reactor. Adjust gas flow so that brown liquid occupies less than ~1/3 space of the chamber. Add triiodide solution. Use 25 mL acetic acid to rinse the triiodide solution vial and transfer all liquid to reaction chamber (i.e., total 40 mL acetic acid + 4 mL triiodide solution).
   b. Connect the outlet of base trap with the filter (analyzer inlet). Adjust gas flow, reading on pressure gauge downstream to base trap should NEVER exceed 1 psi, otherwise you run the risk of breaking the reaction chamber within the NO analyzer! Normally, prior to tubing connection, there’s slight negative pressure due to NO analyzer sample flow (suction).

1.6 Standard Curve and Sample Measurement
   b. See example spreadsheet for sample injection, check standard selection, data recording and calculation. (“ExampleDataSheet20140701”)

1.7 Data Collection and Analysis
   a. After NO analyzer is warmed up, MEAS will appear on the top right-hand corner of the front panel. Open data recording software (Excel with Macro built in). Under Add-on panel, start measurement. Wait till baseline stable before injecting the first standard. Do not use Excel at all during data collection – it stops the data collection...
   b. Current data recording parameters (usually doesn’t need to be changed)
c. See example spreadsheet for data recording and calculation (“ExampleDataSheet20150701”)
d. Copy data (time and reading columns) into a separate excel file, save as .csv (comma delimited)
e. Open Chromprocessor on desktop
f. Import files: Import from Matrix directory the .csv file and follow prompts doing the least possible. Rare occasions: import error if there’s a cell missing in the data file. Find it and remove the line. Re-import the updated .csv file.
g. Smoothing: Set filter frequencies to 0% V1 and 7% V2, then press green check mark
  ✓ Baseline correction: Edit nodes using red squares to drag baseline to peak edges, then press green check
h. Under Analysis menu
  ✓ Select peak picking – auto
  ✓ Integration – manual: Drag red bars to surround peaks and read off areas

1.8 System Shut-down

a. Disconnect reaction chamber to base trap. Make sure immediately drain reaction solution from the reaction chamber, otherwise it may gush into condenser…

b. **Make sure you disconnect tubing before pressing the SYS button!** Otherwise base trap solution will be sucked into the vacuum line connecting to the NO analyzer.

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c. CLD 88 Y et: press SYS button, and then Yes on front of instrument. Wait for flashing signal on the front screen to switch off.
d. Turn off both water baths.
e. Rinse the bottom quartz filter by fill in DI water from the gas inlet port to dissolve crystals precipitate out at the bottom of the reaction chamber.
f. Disconnect analyzer inlet from the pressure gauge and wrap with clear zipper storage bag
g. Turn off N₂ gas.

2.0 Specifications/Features
- Measuring range: 0 – 5000 ppb
- Minimum detectable concentration: 0.05 ppb
- Noise at zero point (1 sigma): 0.025 ppb
- Linearity in range: ± 1%
- Lag time: < 1 sec
- Rise time (0-90%): < 30 sec
- Temperature range: 5 – 40 °C
- Humidity tolerance: 5-95% R.H.
- Sample flow rate: 0.3 L/min or 0.1 L/min with external restriction
- Input pressure: ambient
- Internally generated dry air use for O₃ generator

3.0 User Requirements
The Eco Physics CLD 88Y NO Analyzer must be used by authorized personnel only. All authorized users are expected to read and understand this SOP and follow the operation instructions carefully. No unauthorized user may operate this NO Analyzer unless accompanied by an authorized user. All visitors must be briefed on proper safety protocol and must wear appropriate personal protective equipment. To become an authorized user, one must:

1. Complete Environment, Health & Safety (EH&S) training
2. Complete initial orientation and training for the Materials Characterization Laboratory
3. Receive training on this piece of equipment from lab personnel
4. Schedule equipment time using the calendar
5. Read and fully understand this SOP
4.0 General Safety

4.1 Required Personal Protective Equipment
Users must wear lab coats, safety glasses, and gloves. Shorts, open-toed shoes, high heels, and skirts, are forbidden.

4.2 Emergency Procedures and Contacts
For non-life threatening emergencies: notify the MCL facility manager and your PI immediately.
Facility manager: Zongmin (Shirley) Bei, Ph.D.
Office: 109B Furnas Hall, Tel: (716) 645-5165, Cell: (585) 354-5623
Email: zongminb@buffalo.edu
or for police / ambulance, call 645-2222

In case of fire or other life threatening emergency: Exit the laboratory through an emergency exit door. Pull one of the fire alarms located in the main hallway. Dial campus police / ambulance at 645-2222.

4.3 University after hours laboratory use policy
No working alone, use the buddy system!

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