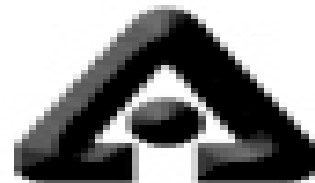


Nitrogen Dioxide (NO_2), Peroxyacyl Nitrates (PANs) and Black Carbon (BC) --- Measurements



Luis A. Cuadra-Rodríguez
Jeffrey S. Gaffney and Nancy A. Marley
Environmental Research Division, Argonne
National Laboratory

Outline

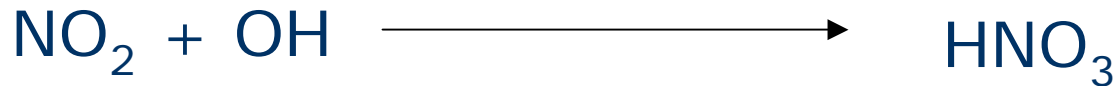
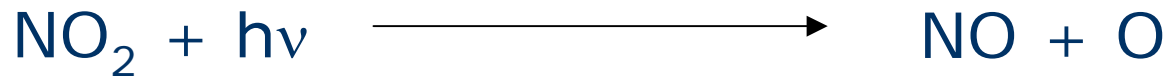
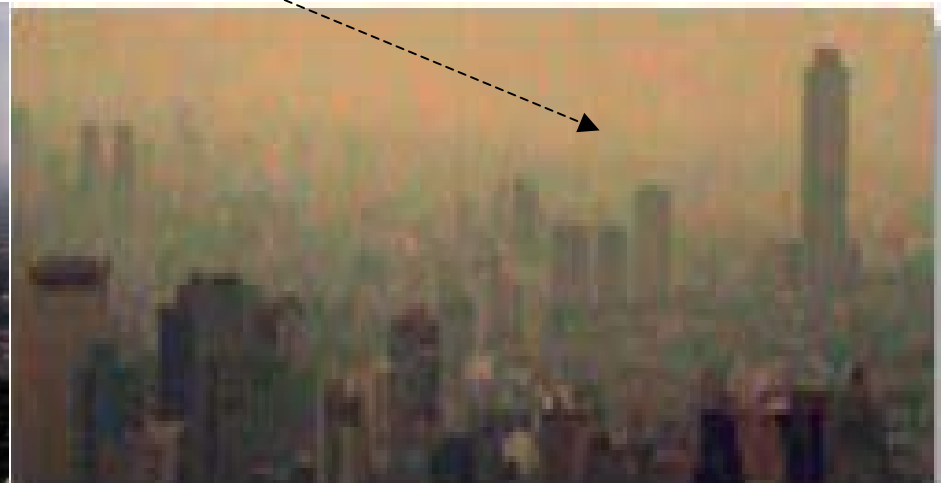
- Introduction
- Instrument design for NO₂ and PAN measurements
- Methods
- Results
- Summary
- Future work
- Acknowledgements

Introduction

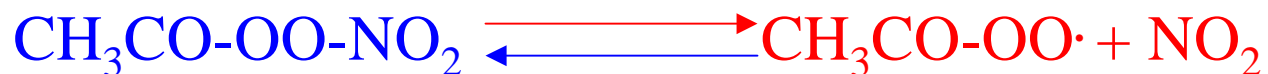
Nitrogen dioxide (NO_2) and peroxyacyl nitrates (PANs) are pollutants that can lead to local and regional scale effects. NO_2 photolysis leads to the formation of ozone and, oxidation of NO_2 by hydroxyl radical leads to the formation of nitric acid.

PANs can be defined as stored peroxy radical and NO_2 , and have the general chemical structure **$\text{RC}=\text{OO}-\text{O}-\text{NO}_2$** (PAN, PPN, PBN). PANs can transport the NO_2 for long distances because of its properties and the temperature dependence equilibrium within these species.

Also NO_2 and PANs are important species in the photochemical smog formation



Thermal Equilibrium

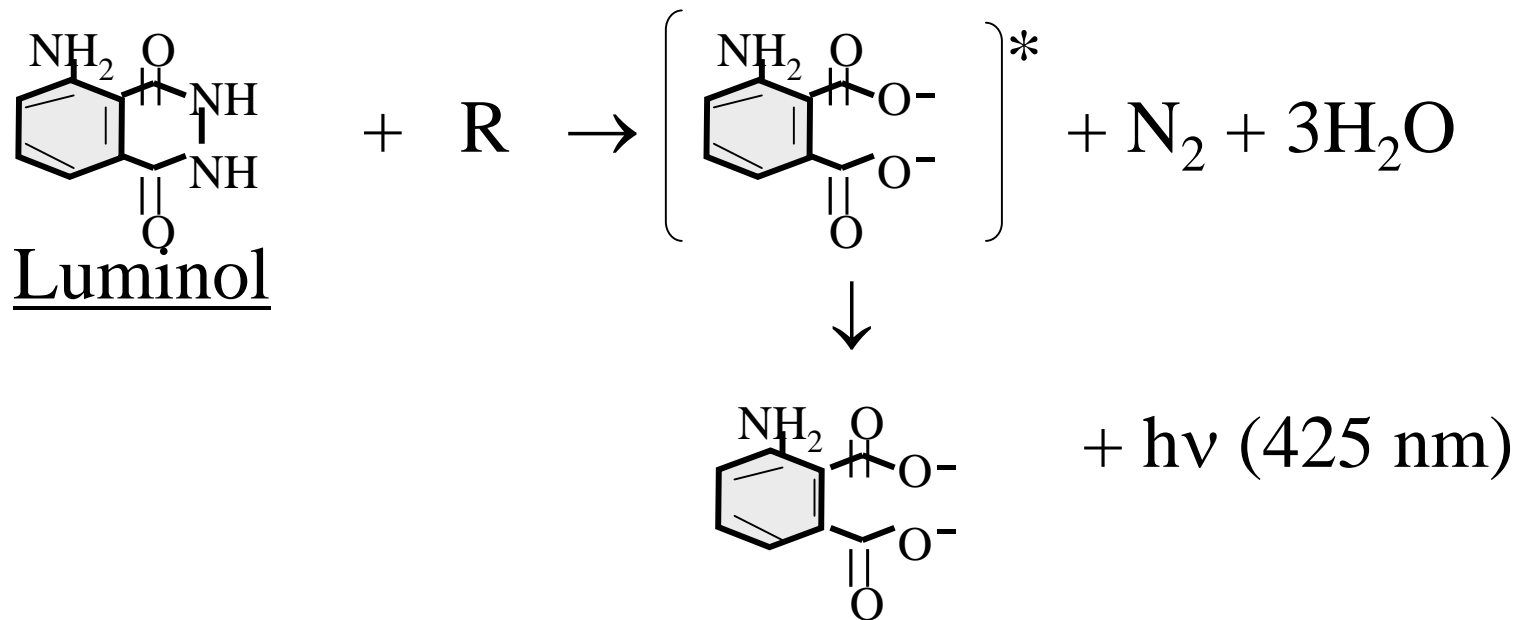


Black or Elemental Carbon

- Insoluble part of aerosols.
- Affect directly the visibility.
- Is a strong absorber of visible and infrared radiation, leading to heating of the atmosphere. But it can also cool the atmosphere by scattering of radiation.
- It is expected in urban areas that the heating effect predominates.
- Human activities: **fossil fuel** burning for energy, automobiles (gasoline and **diesel**), industry, in summary all **combustion** sources.

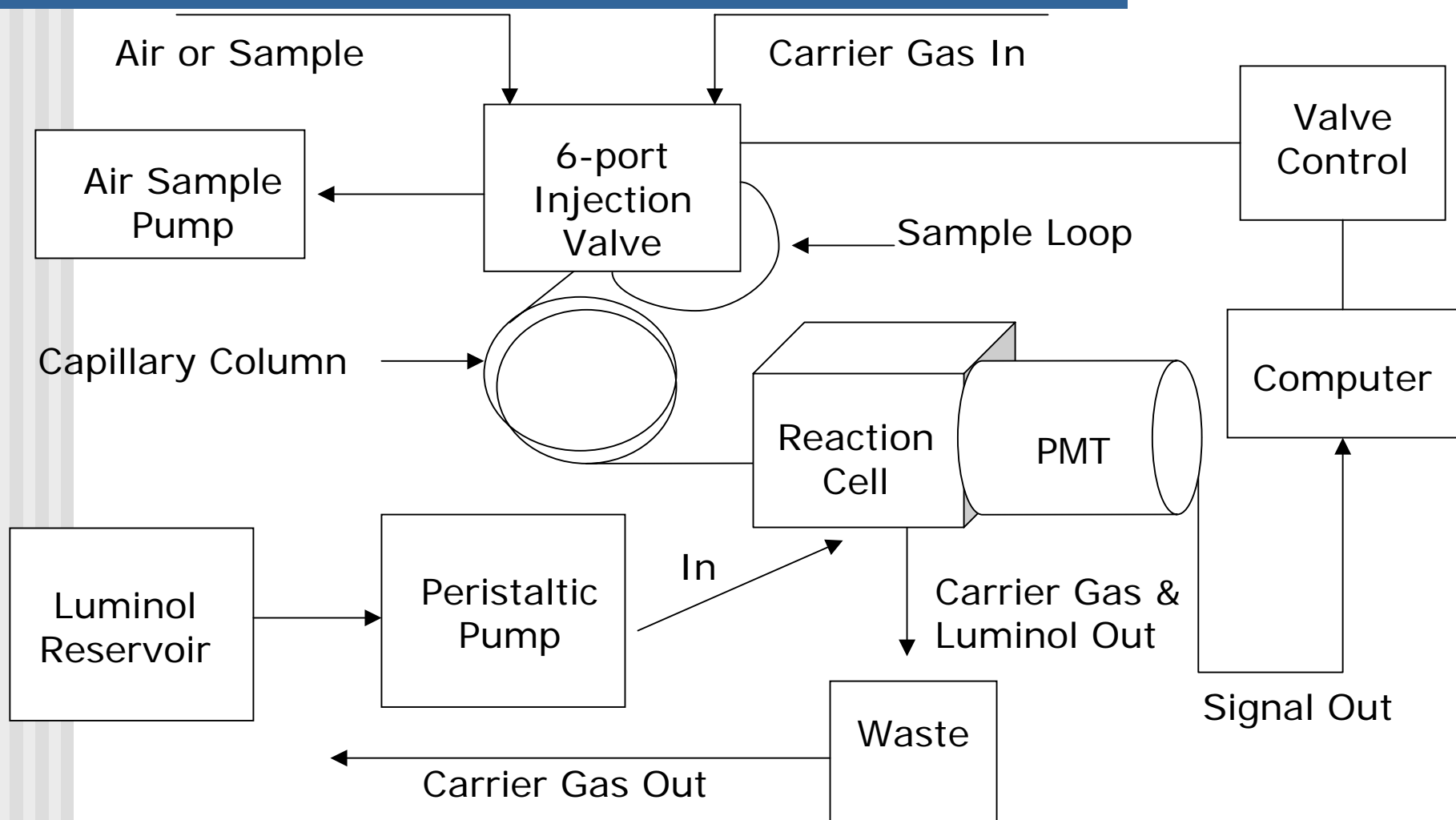


Chemiluminescent Reaction with Luminol



R can be NO_2 , PANs, H_2O_2 , enzymes, metal ions, carbohydrates and can be selected by changing the pH, ionic strength or including a catalyst in the luminol solution.

Instrument Design

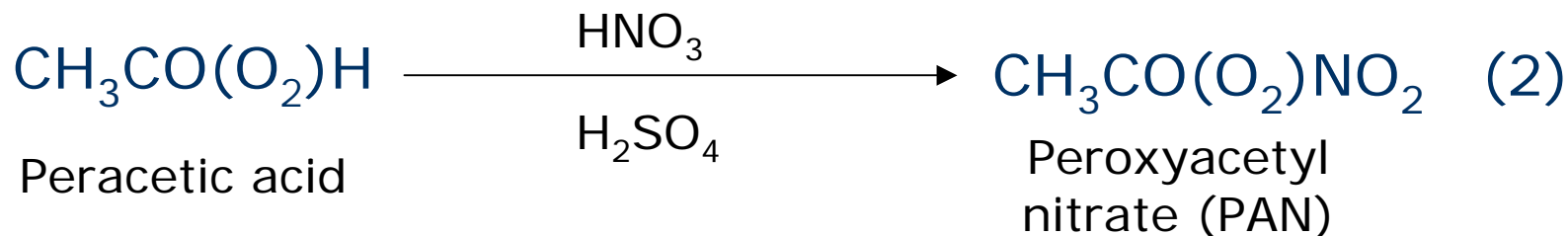
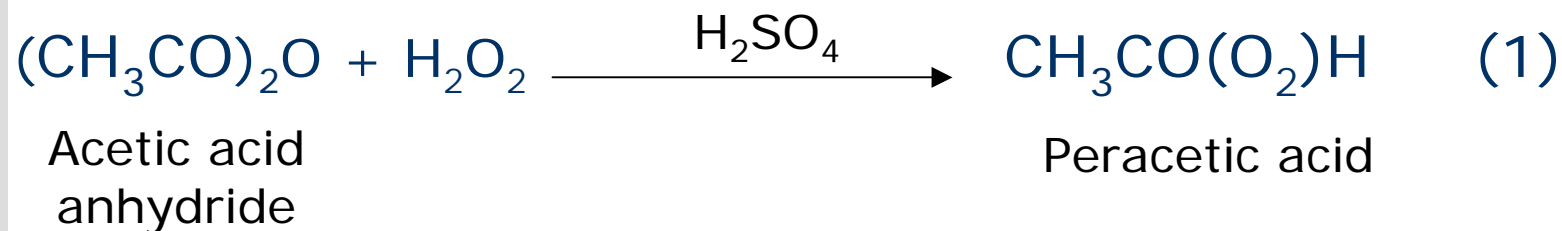


Methods

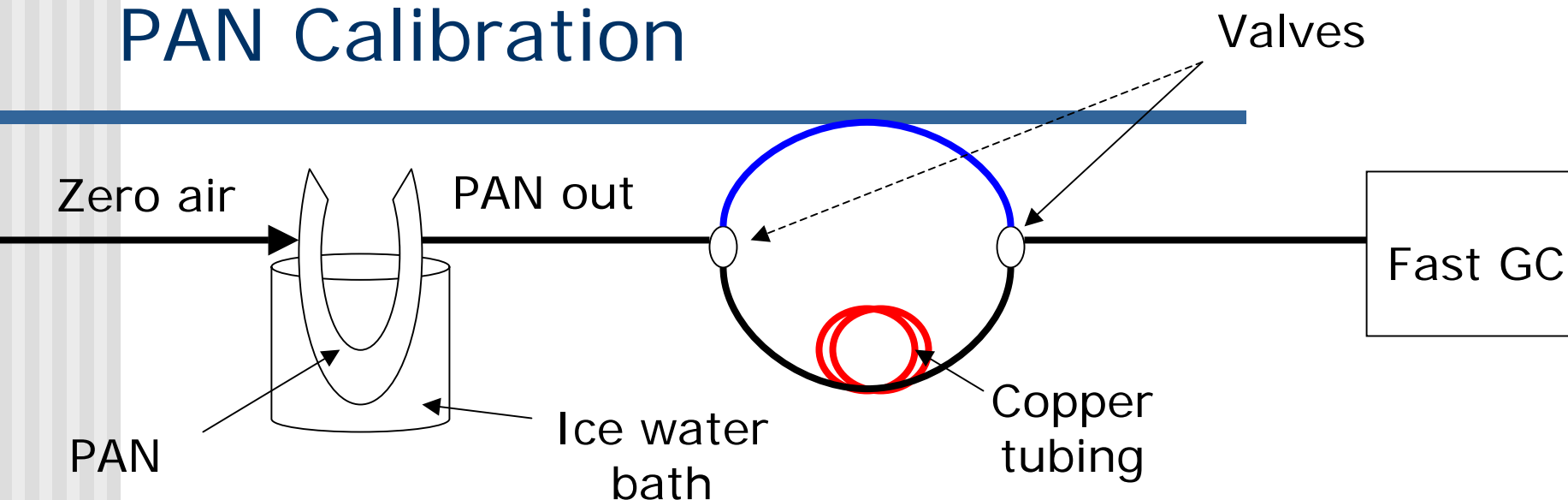
NO₂ Calibration

- NO₂ standard diffusion wafer tube that release 150 ng/min. at 35 °C was used. The dilution was made with a Dynacalibrator Model 190 to vary concentrations.

Synthesis- Peroxyacetyl Nitrate (PAN)



PAN Calibration

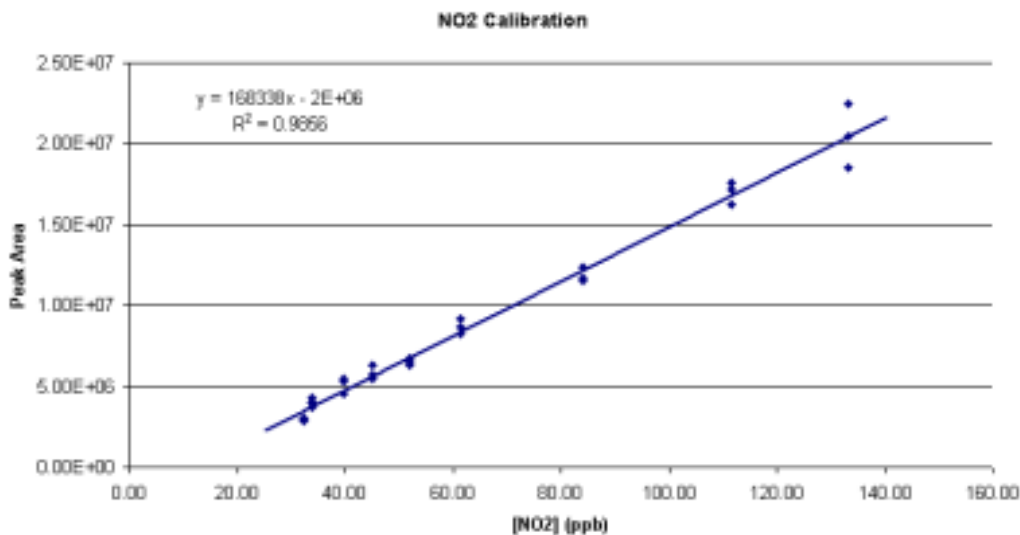


Black Carbon

- BC measurements were taken with an aethalometer with 7 different channels (radiation wavelengths)

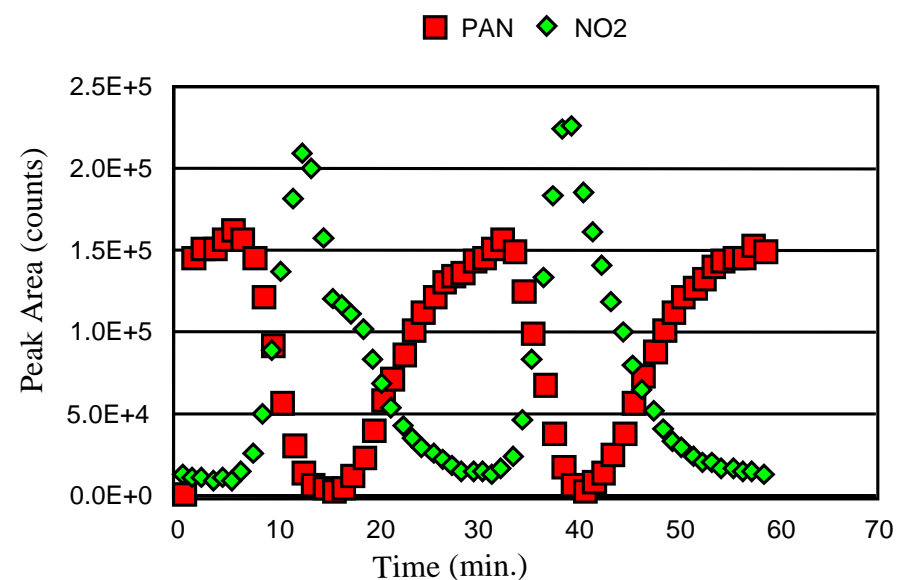
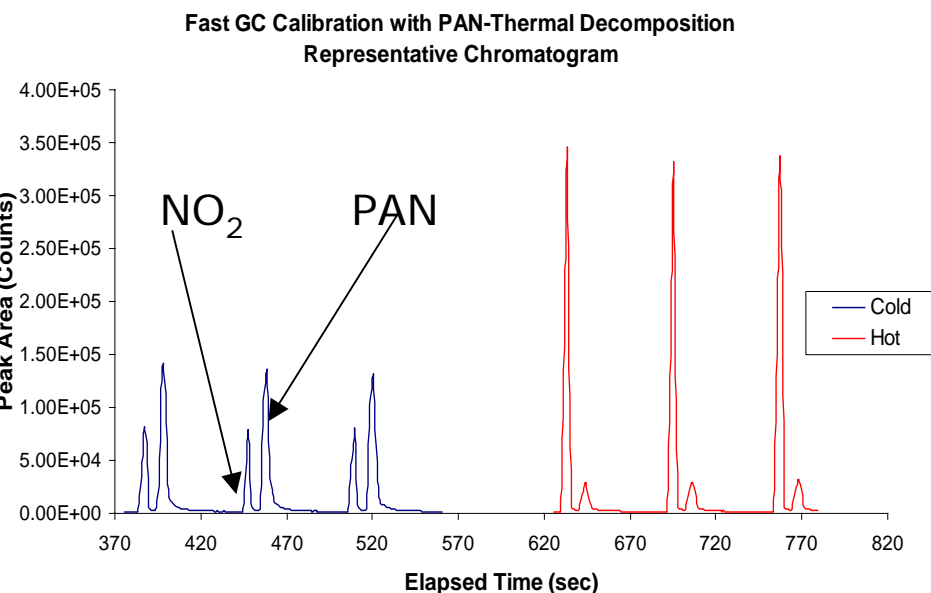


NO₂ calibration

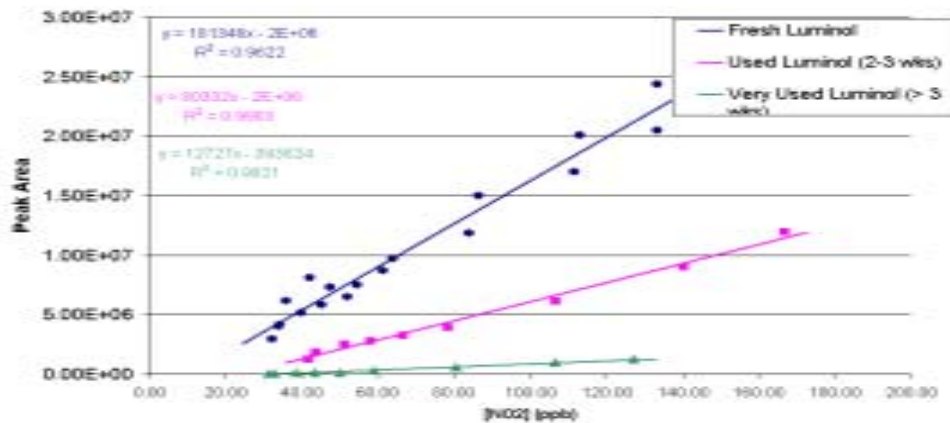


- Sensitivity of the instrument is in the order of 10^5 counts/ppb.
- The NO₂/PAN ratio gives a relative sensitivity between 1.04-2.53 with an average of 1.5

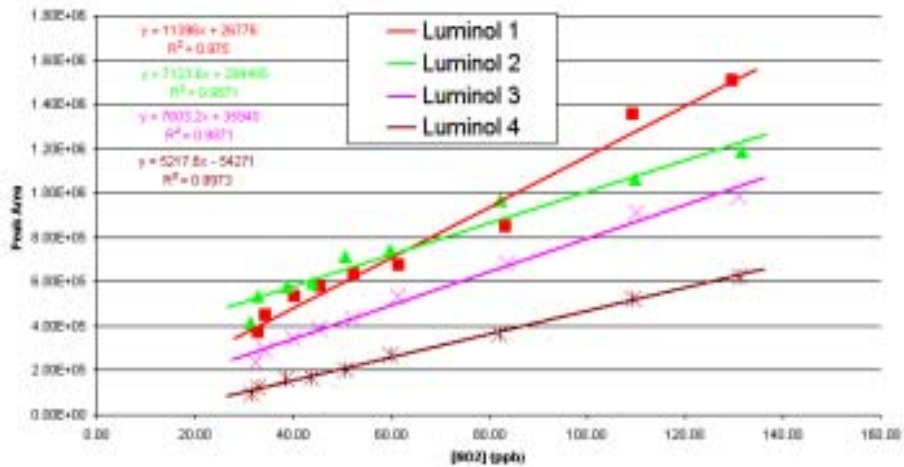
PAN calibration



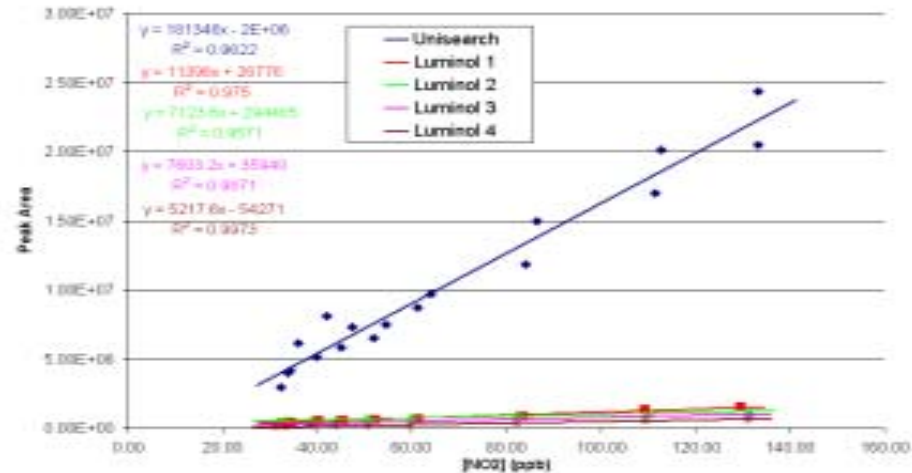
Fast GC/Luminol Calibration with NO₂



Fast GC/Luminol Calibration with NO₂ and Different Luminol Solutions



Fast GC/Luminol Calibration with NO₂ and Different Luminol Solutions



Luminol 1 (Luminol 1 x 10⁻³ M, KOH 0.5M)

Luminol 2 (Luminol 1 + 0.2 M Na₂SO₃)

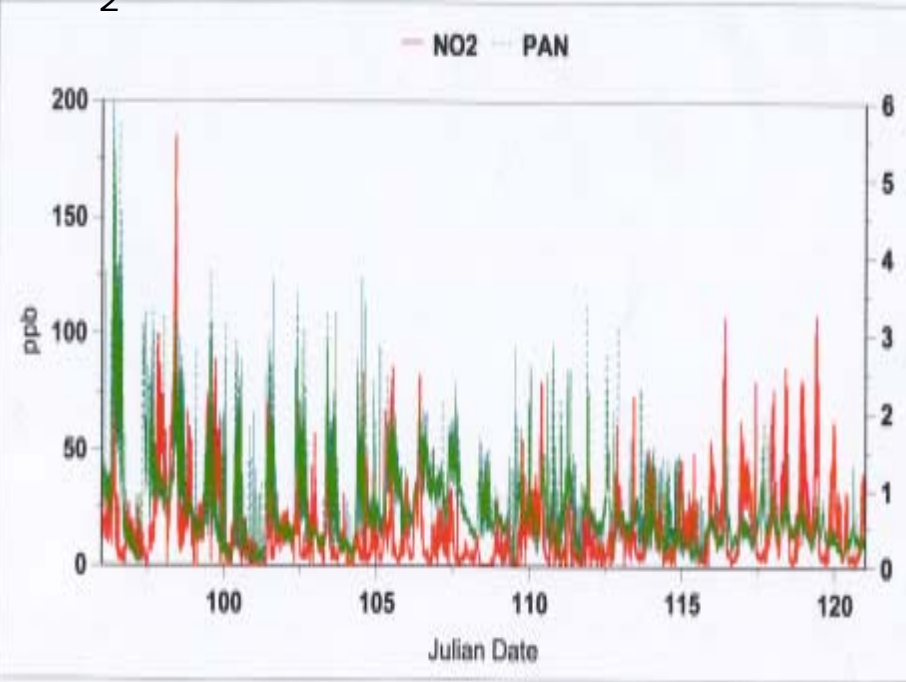
Luminol 3 (Luminol 1 + 0.01 M EDTA)

Luminol 4 (Luminol 2 + 0.01 M EDTA)

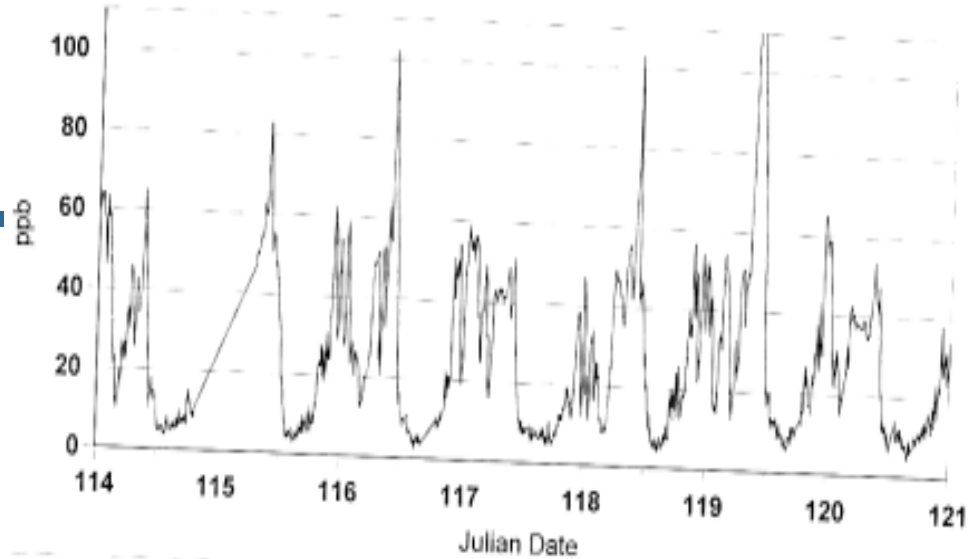
NO₂ and PAN

NO₂

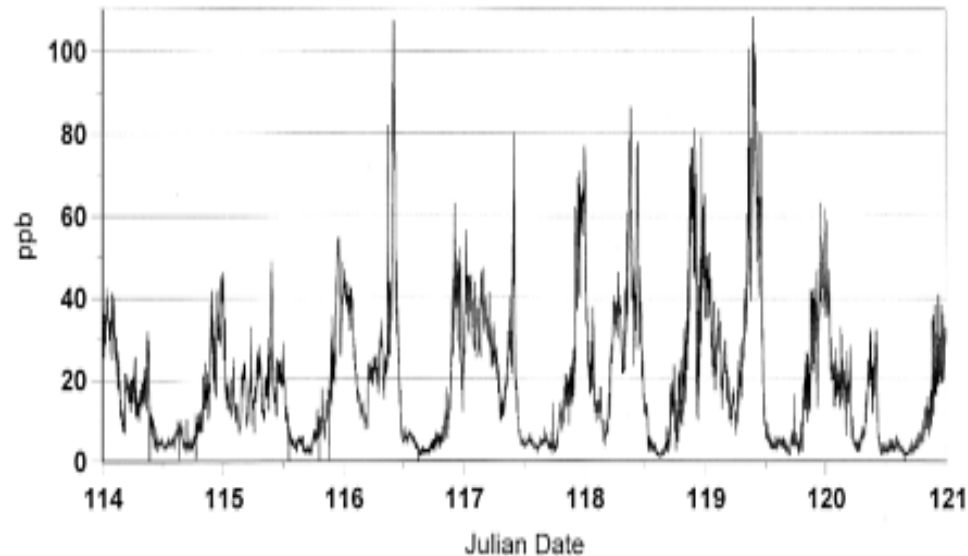
PAN



DOAS NO₂



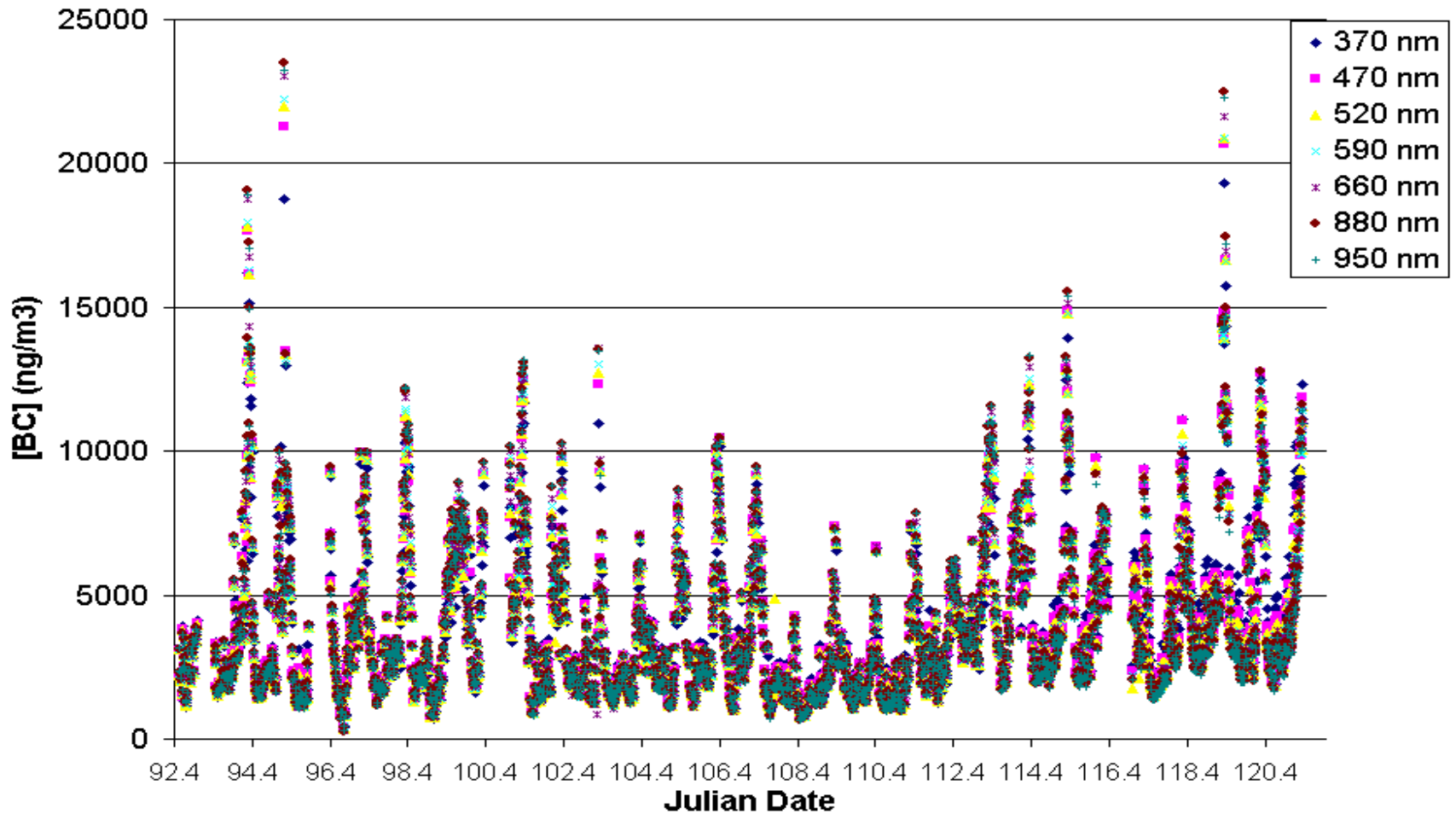
NO₂



Comparison of Fast GC/
Luminol (data point) with
the DOAS (2 km)

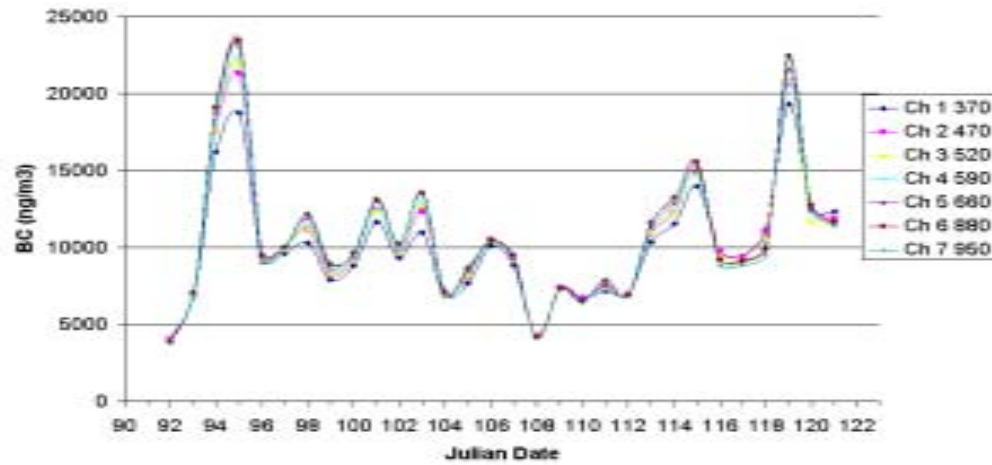
Black Carbon

BC Mexico-ANL, CENICA, MCMA 2003



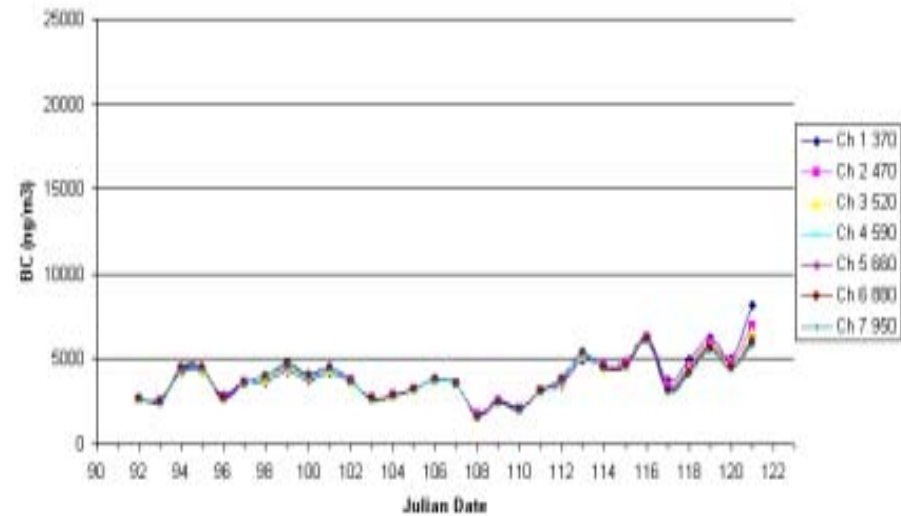
Daily Maximums

BC Maximums for MCMA



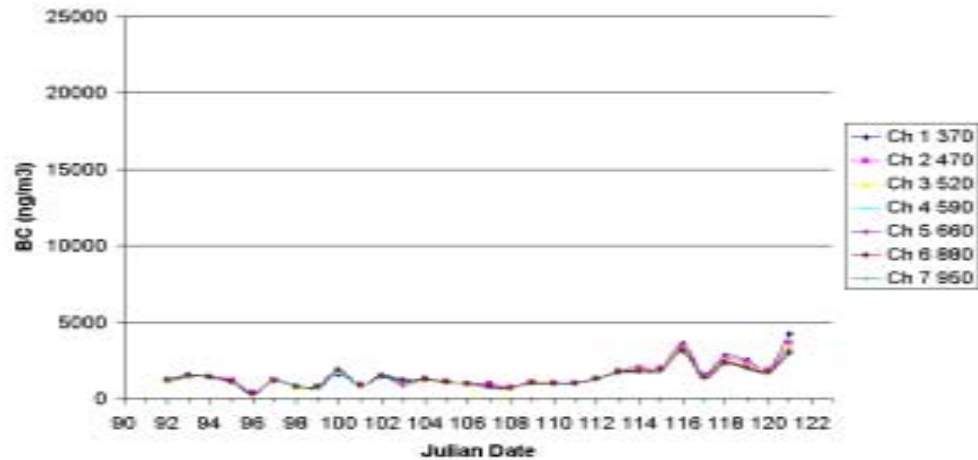
Daily Averages

BC Average for MCMA



Daily Minimums

BC Minimums for MCMA



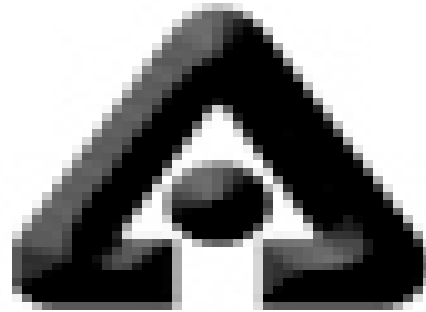
Summary

- The Fast GC/ Luminol instrument have demonstrated a high sensitivity, in the sub-ppb range.
- Comparisons made with DOAS suggest that the the air is reasonable well mixed in CENICA site and also makes clear the reliability of the instrument.
- Black carbon peak in Mexico is 5 times greater than Chicago or other big cities, minimums 9-10 times greater than backgrounds concentrations.
- The effect of black carbon, whether is heating or cooling the atmosphere, we can conclude that is directly affected by human activity in urban areas.

Future Work

- Continue making new luminol solutions with different concentrations NaSO_3 , EDTA, KOH, etc. compare the response with the solutions acquired from Unisearch and improve the sensitivity of the instrument.
- Synthesize other PANs like peroxypropionyl nitrate (PPN) and peroxybutyryl nitrate (PBN) and calibrate the instrument with a mix of the three PANs.
- Take measurements in Chicago city including ozone (and other like UV-B radiation, NH_3 , etc.) measurements to compare with the Mexico city site.

Acknowledgements



DOE

ANL

GCEP

