Instrumentation

O_3
Chain Initiation, Final Product
UV-Spectrophotometry

NO
Primary Pollutant, Oxidant Precursor
BNL 3-Channel Instrument

CO
Fuel, Product, Tracer
BNL Modified Instrument
BNL Fast VUV Instrument

Data Aquisition
Real-Time Display
Instrument Control, Cals

NO_2
Catalyst
BNL 3-Channel Instrument

HNO_3, Particulate NO_3^-
Termination & Removal
BNL Filter Pack

Operations
Instrument Prep and Installation,
Data Reduction,
Data Validation,
Archive and Dessimination

SO_2
Tracer, Source Indicator
BNL Modified Pulse Fluorescence

NO_y
Reactive N Mass Balance
BNL 3-Channel Instrument

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Recent Field Program Participation

SOS '95, Nashville, TN	Results in press
ACP '95, Westhampton Beach, NY	Results in press
ACP '96, Westhampton Beach, NY	Ongoing analysis
NARSTO-NE '96, Westhampton Beach, NY	Ongoing analysis
NARSTO Ground Site, BNL, NY	Ongoing measurements
Phoenix '98, Phoeniz, AZ	Scheduled for summer '98

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Data Archive

Files archived on CD-ROM and archived on server

Final form data available to public at ftp://aerosol.das.bnl.gov/pub
Also available on CD-ROM by request

Multiple data formats

- ASCII Flat File (tab delimited)
- QuattroPro V7/8
- Lotus Symphony V2.0

Processed data with only valid measurement periods reported

Uniform style across formats to facilitate retrieval

Row 1:	file name
Row 2:	date
Rows 4-6:	contact information
For each column:	
Row 7:	current revision
Rows 9-12:	instrument information
Rows 14-19:	free form comments on data
Rows 21-24:	available for calibration constants
Rows 35-36:	signal identification
Row 37:	units
Rows 40-end:	data (blanks for missing data)

Recent Publications Using This Instrumentation

NARE 1993

Kleinman, L.I., P.H. Daum, J.H. Lee, Y-N. Lee, J. Weinstein-Lloyd, S.R. Springston, M. Buhr, and B.T. Jobson, Photochemistry of O_3 and Related Compounds Over Southern Nova Scotia, J. Geophys. Res., (in press), 1998.

SOS 1994

Williams, E.J., K. Baumann, J. M. Roberts, S.B. Bertman, R.B. Norton, F.C. Fehsenfeld, S.R. Springston, L.J. Nunnermacker, L. Newman, K. Olszyna, J. Meagher, B. Hartsell, E. Edgerton, J. Pearson, and M.O. Rodgers, Intercomparison of NO_y Measurement Techniques, submitted to *J. Geophys. Res.*, 1997.

Baumann, K., W.M. Angevine, G.J. Frost, P.C. Murphy, R.B. Norton, D.D. Parrish, J.M. Roberts, T.B. Ryerson, B.T. Jobson, E.J. Williams, F.C. Fehsenfeld, S.R. Springston, S.B. Bertman, B. Hartsell, Ozone Production in an Urban Plume: Results from the 1994 Hendersonville Study, submitted to *J. Geophys. Res.*, 1997.

SOS 1995

Imre, D., P.H. Daum, L. Kleinman, Y-N Lee, J. H. Lee, L. J. Nunnermacker, S. R. Springston, L. Newman, J. Weinstein-Lloyd, Sanford Sillman, Characterization of the Nashville urban plume on July 3 and July 18, 1995: II. Processes, Efficiencies, and VOC and NOx ILmitation, submitted to *J. Geophys. Res.*, 1997.

Kleinman, L., P.H. Daum, J.H. Lee, Y-N. Lee, L.J. Nunnermacker, S.R. Springston, L. Newman, J. Weinstein-Lloyd, S. Sillman, Dependence of Ozone Production on NO and Hydrocarbons in the Troposphere., Geophys. Res. Let., (in press), 1998.

Kleinman**,** L., P. Daum, D. Imre, C. Cardelino, K. Olszyna, and R. Zika, Trace Gas Concentrations and Emissions in Downtown Nashville during the 1995 SOS/Nashville Intensive, submitted to *J. Geophys. Res.*, 1997.

Lee, Y.-N., X Zhou, L. J. Nunnermacker, S. R. Springston, L. I. Kleinman, D. Parrish, J. Holloway, and F. Fehsenfeld, Atmospheric Distribution and Chemistry of Formaldehyde and Several Multi-Oxygenated Carbonyl Compounds during the 1995 Nashville/Middle Tennessee Ozone Study, submitted to *J. Geophys. Res.*, 1997.

Nunnermacker, L.J., D. Imre, P.H. Daum, L. Kleinman, Y-N Lee, J.H. Lee, S.R. Springston, L. Newman, J. Weinstein-Lloyd, W.T. Luke, R. Banta, R. Alvarez, C. Senff, S. Sillman, M. Holdren, G.W. Keigley, X. Zhou, Characterization of the Nashville Urban Plume on July 3, and July 18, 1995: 1. O3 Production Efficiency, Kinetic Analysis, and Hydrocarbon Apportionment., submitted to *J. Geophys. Res.*, 1997.

Nunnermacker, L.J., P.H. Daum, L. Kleinman, D. Imre, J. Weinstein-Lloyd, S.R. Springston, Y-N. Lee, L. Newman, J.H. Lee, NO_y Lifetimes and O_3 Production Efficiencies in Urban and Power Plant Plumes: Analysis of Field Data., EOS, Transactions, AGU **78**(46), 1997 Fall Meeting, abstract # A11A-16, pg. F60.

Recent Publications Using This Instrumentation

SOS 1995 (continued)

Weinstein-Lloyd, J., J. H. Lee, P. H. Daum, L. I. Kleinman, L. J. Nunnermacker, S. R. Springston, L. Newman, Measurements of Peroxides and Related Species During the 1995 Summer Intensive of the Southern Oxidants Study in Nashville, TN, submitted to *J. Geophys. Res.*, 1997.

Valente, R. J., R.E. Imhoff, R.L. Tanner, J.F. Meagher, P.H. Daum, R. M. Hardesty, R.M. Banta, R.J. Alvarez, R. McNider, N. Gillani, Ozone Production During an Urban Air Stagnation Episode Over Nashville, TN, In Press.

Hubler, G., R. Alvarez, P. Daum, R. Dennis, N. Gillani, L. Kleinman, W. Luke, J. Meagher, D. Rider, M. Trainer, R. Valente, An Overview of the Airborne Activities During the SOS 1995 Nashville/Middle Tennesee Ozone Study, J. Geophys. Res., In Press.

Sillman, S., D. He, M. Pippen, P.H. Daum, J.H. Lee, L.I. Kleinman, J. Weinstein-Lloyd, Model Correlations for Ozone, Reactive Nitrogen and Peroxides for Nashville in Comparison with Measurements: Implications for O3-NOx-Hydrocarbon Chemistry, J. Geophys. Res., In press.

ACP 1995

Berkowitz, C.M., J.D. Fast, S.R. Springston, R.J. Larsen, C.W. Spicer, P.V. Doskey, J.M. Hubbe, R. Plastridge, Elevated Photochemical Layers over the Northeast United States, submitted to *J. Geophys. Res.*, 1997.

NARTSO NE 1996

Kleinman, L., P.H. Daum., D. Imre, P. Klotz, J.H. Lee, Y-N. Lee, L.J. Nunnermacker, S.R. Springston, J. Weinstein-Lloyd, L.Newman, Ozone Production in the New York City Urban Plume., EOS, Transactions, AGU **78**(46), 1997 Fall Meeting, abstract # A42A-9, pg. F118.

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Environmental Chemistry Division

Nitrogen Species

Species	Importance	Technique	Instrument	Precision/ Time Response
NO	Primary pollutant, key to photochemical oxidant production	Chemiluminescence	Brookhaven 3-Channel Instrument	<10 pptv (@30 s) < 1 s response time
NO2	Principal O_3 precursor, major NO_y constituent	UV-photolysis followed by chemiluminescence	Brookhaven 3-Channel Instrument	<50 pptv (@30 s) < 4 s response time
Total NO_y	Quantifies total odd-nitrogen species	Heated Mo catalyst followed by chemiluminescence	Brookhaven 3-Channel Instrument	<50 pptv (@30 s) ~1 s response time
Total $NO_3^=$	Includes HNO_3 and aerosol $NO_3^=$ as final oxidation products	1) Measured by difference following selective removal with nylon filter	Brookhaven 3-Channel Instrument	~50 - 100 pptv, 30 s
		2) Glass coil scrubber/ ion chromatography	Brookhaven Instrument	0.3 pbbv, 3 min
Aerosol $NO_3^=$	Removal species	Quartz filter	Brookhaven filter pack	~ 20 pptv, 2h
HNO_3	Dry deposition	NaCl filter	Brookhaven filter pack	~ 5 pptv, 2h
PAN	Major reservoir species, important for transport	Gas chromatography/ Electron Capture Detection	Shimadzu GC/ECD	~10 - 50 pptv, 30 min

Environmental Chemistry Division

Gaseous Species

Species	Importance	Technique	Instrument	Precision/ Time Response
O_3	principal photo oxidant	1) UV photometry	TECO Model 49	~2 ppbv, 30 s
		2) Chemiluminescence	AID Model 560	~5 ppbv, 1 s
SO_2	primary pollutant	1) Pulsed fluorescence	TECO Model 42S, BNL modified	~200 pptv, 15 s
		2) Glass scrubber/ derivatization/ fluorimetry	BNL Instrument	20 pptv, 1 min
CO	Mobile emission source, tracer	Gas-filter correlation	TECO Model 48, BNL modified	~10 ppbv, 1 min
Carbonyls	Rxn intermediates in HC oxidation	Glass scrubber/ HPLC of DNPH derivative	BNL Instrument	10 - 20 pptv, 3 min
H_2O_2, MHP, HMHP	Photochemical product	Glass scrubber/ selective derivatization/ fluorimetry	Kok Instrument/ BNL Chemistry	~60 pptv, 1 min
Hydrocarbons	Fuel for ozone production, primary anthropogenic and biogenic emission	Canister/ gas chromatography	Capillary GC	10 - 100 pptv

Environmental Chemistry Division

Sub-Micrometer Aerosols

Species	Importance	Technique	Instrument	Precision/ Time Response
D_p > 3 nm	Aerosol microphysics	Condensation particle counter	TSI 3025	$N^{1/2}$, 1 s
D_p > 10 nm	Aerosol microphysics	Condensation particle counter	TSI 3010	$N^{1/2}$, 1 s
D_p > 15 nm	Aerosol microphysics	Condensation particle counter after drying	TSI 3760	$N^{1/2}$, 1 s

Environmental Chemistry Division

Other Measurements

Species	Importance	Technique	Instrument	Precision/ Time Response
Strong acid	Health, biogenic effects	Quartz filter	Brookhaven filter pack	~300 pptv, 2h
Aerosol $SO_4^{=}$	SO_2 removal	Carbonate filter	Brookhaven filter pack	~20 pptv, 2h
Total UV	Photolytic driving force	Photometry	Eppley pyranometer	0.5 W/m^2, 1 s
b_{scat}	Visibility, particle burden	Integrating nephelometry	mri Model i550	0.05 x $10^{-4}m^{-1}$, 5 s
Meteorological parameters	Local interferences, site representativeness		Climatronics sensor	1 s

Analytical Objectives for FY '98

- Construct VUV Fluorescence Instrument for Carbon Monoxide
  - Instrument based on VUV prototype by Volz and Kley
  - Dielectric mirrors will provide ~50 - 100X more excitation light versus monochromator
  - Sealed lamp for stability over flow-through lamp, no supply gas
  - Performance goal: ▲= 1s, S/N = 50 at 50 ppbv
  - Design weight: <10 kg w/o pump (use reserve capacity of NO_y pump)
- $NO/NO_2/NO_y$ Measurement Capability
  - Reduce background
    - Oil-free pump to eliminate backstreaming contamination
    - Glass pre-reactor vessels with reduced volume
    - Investigate convertor configuration to minimize cold spots
  - Increase specificity using dual convertors (NO_y/NO_y^*)
  - Investigate inlet transmission of aerosol and HNO_3

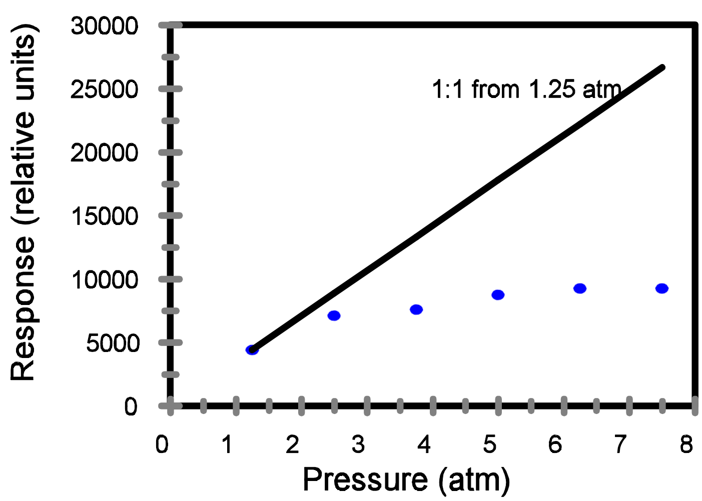
CO Measurement by NDIR

Current commercial instrument modified:

- Flow control (to allow standard addition)
- Pressure control (for altitude stability)
- Temperature control to increase baseline stability

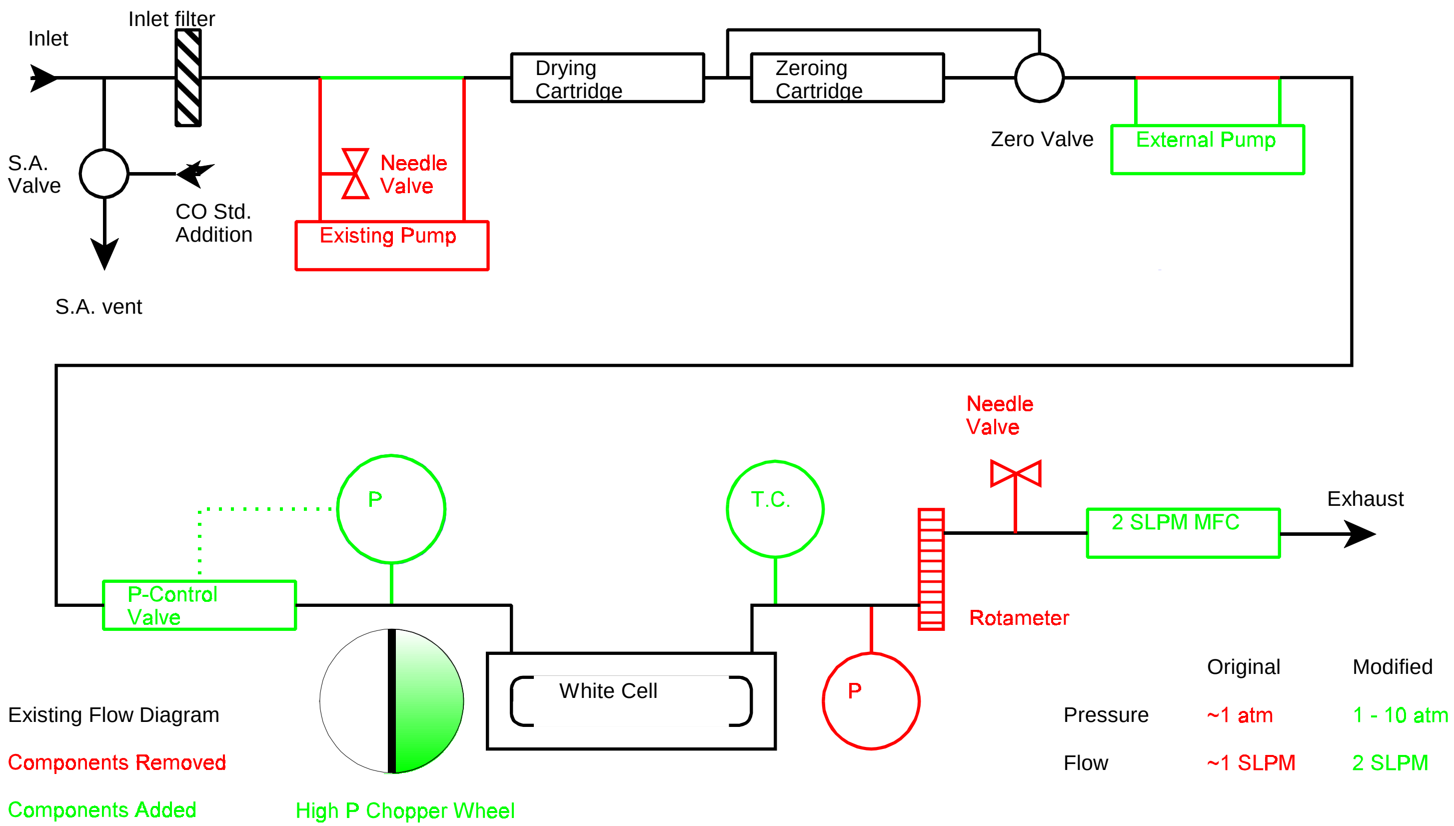
Insufficient sensitivity (MDL = 20 ppbv) and slow response (▲= 20 - 30 s)

To further increase sensitivity, pressurized flow cell implemented (P_{cell} = 1 -10 atm)



Conclusion: Pressure broadening of CO bands causes roll off of sensitivity at higher pressures

NDIR Instrument Modifications (TEI Model 48)



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CO Measurement by VUV Fluorescence

Established principle for aircraft-based measurments

Volz & Kley, J. Atmos. Chem. **2** (1985) 345-57.
Gerbig et. al., JGR **101** (1996) 29229-38.
Active use by NOAA Aeronomy Laboratory, Boulder, CO.

Inherently high sensitivity and selectivity

Better performance than non-dispersive infrared (such as TEI Model 48)

	VUV Fluor. (NOAA)	NDIR
1-? detection at 300 ppbv	<3 ppbv @1 s	~20 ppbv @~20 s
time response	<1 s	~20 s

Negligible H_2O interference with proper wavelength selection

Novel features of proposed instrument

Sealed lamp (vs. flow lamp) will eliminate reagent cylinder, reduce effect of ambient conditions. Reference photodiode to monitor I_0

Three dielectric mirrors for narrow excitation band pass
- Greatly reduced weight (vs. VUV monochromator)
- ~50-200X more light for enhanced S/N

Deep-elliptical fluorescence cell for better light collection

Particulate filter to minimize Mie scattering

Anticipated deployment: Fall '98

Planned VUV Fluorescence Detector for Carbon Monoxide