
Texas Carbon
Smorgasboard
Sandy Dasgupta
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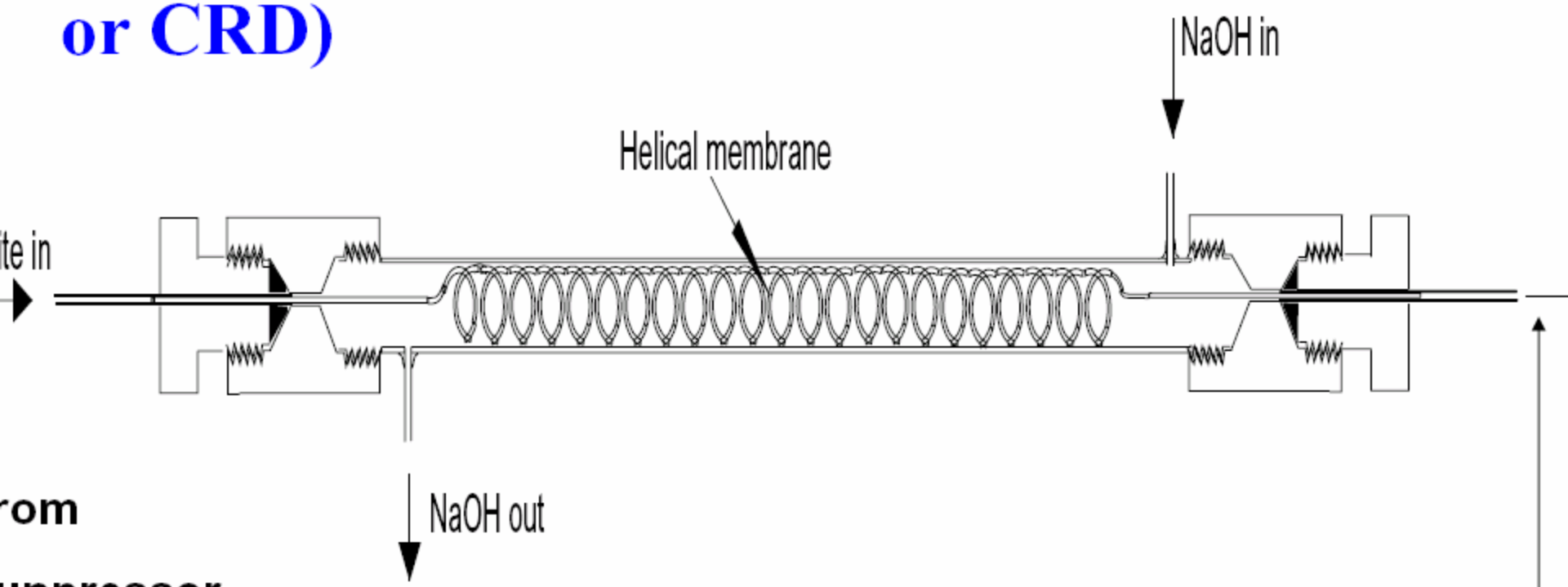
- **CO_2 : Removal and Ion Chromatography**

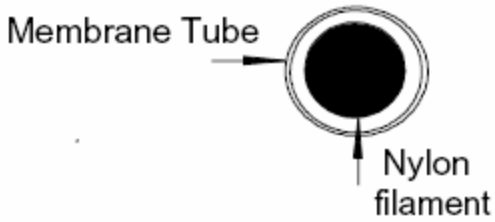
- **A size-speciating multi-λ Aethalometer**
  Wavelength-discriminating Aethalometric Size-Discriminating Particle Sensor (WASPS)
  Excellent correlation of EC with low wavelength aethalometry

- **An alternative to thermooptical carbon speciation: Photo Assisted Stepwise Wet Oxidation and CO_2 Sensing (PASWOCS)**

- **Carbon dioxide is present in the atmosphere at a concentration of ~400 ppm while one is trying to determine low to sub-ppbv levels of other ionogenic gases.**
- ***It would be a significant advancement to remove CO_2/H_2CO_3 prior to detection***.

Construction of CO_2 removal device(de-CO_2 or CRD)

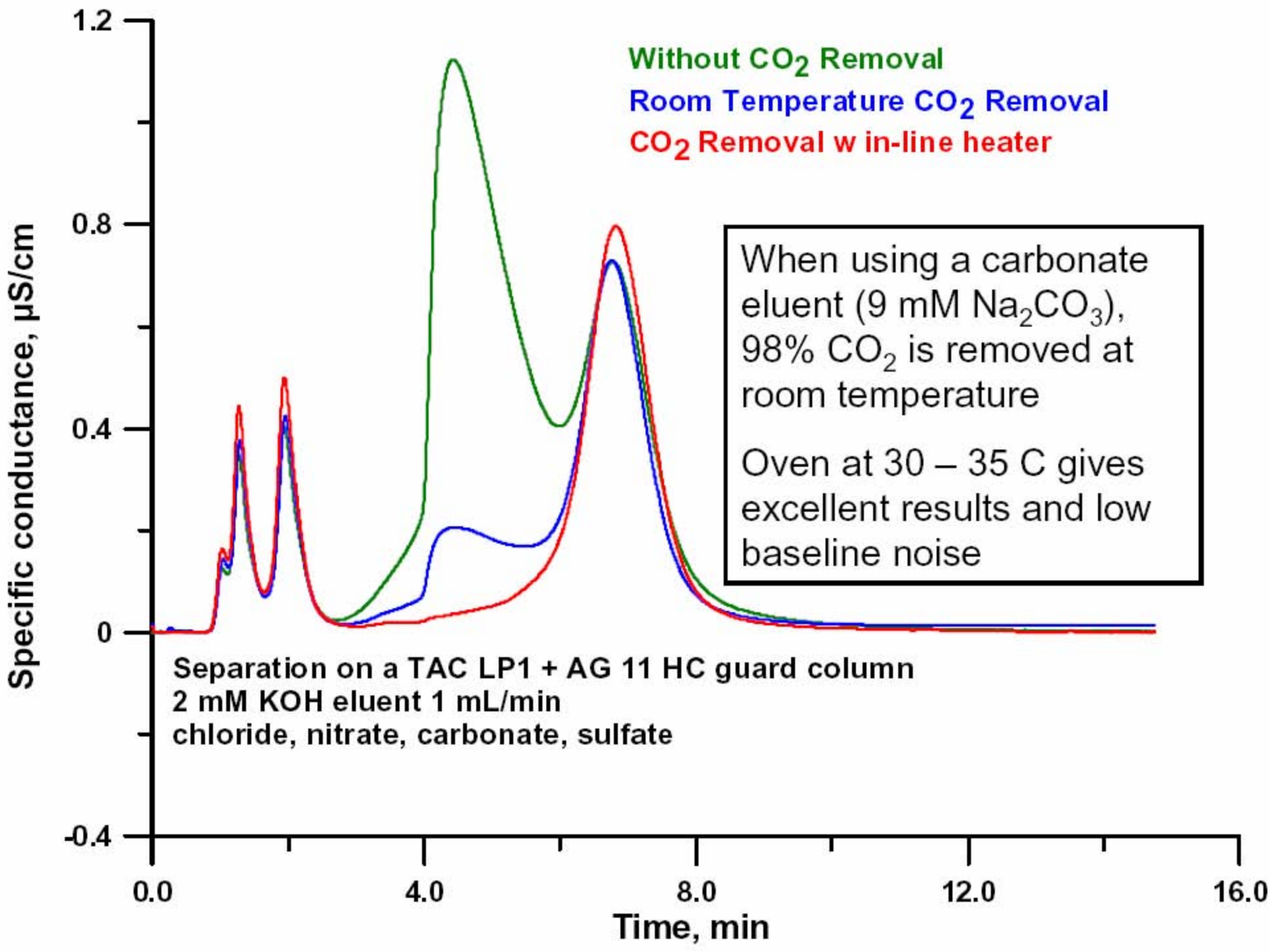


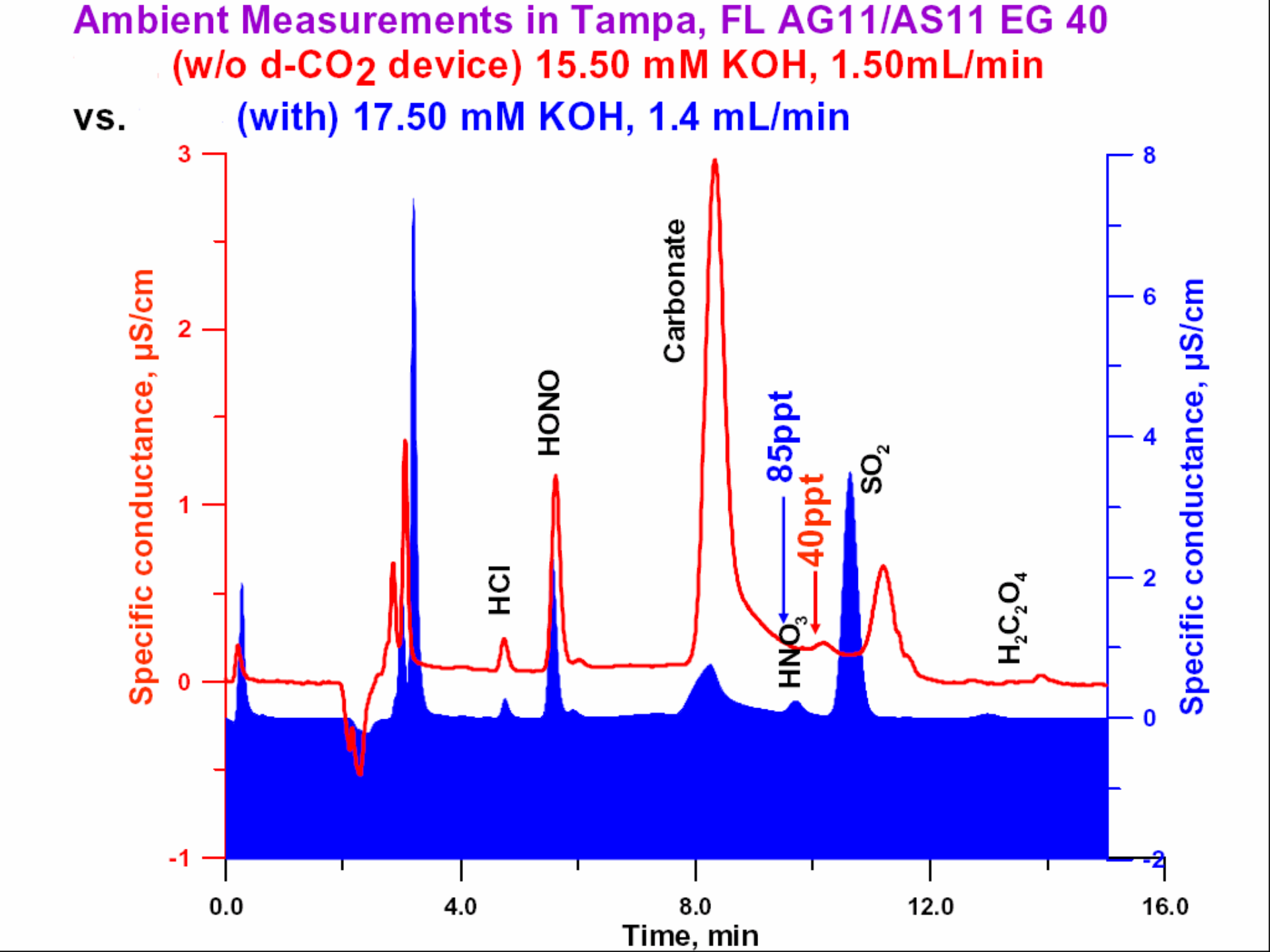


Removal Efficiency of different CRDs

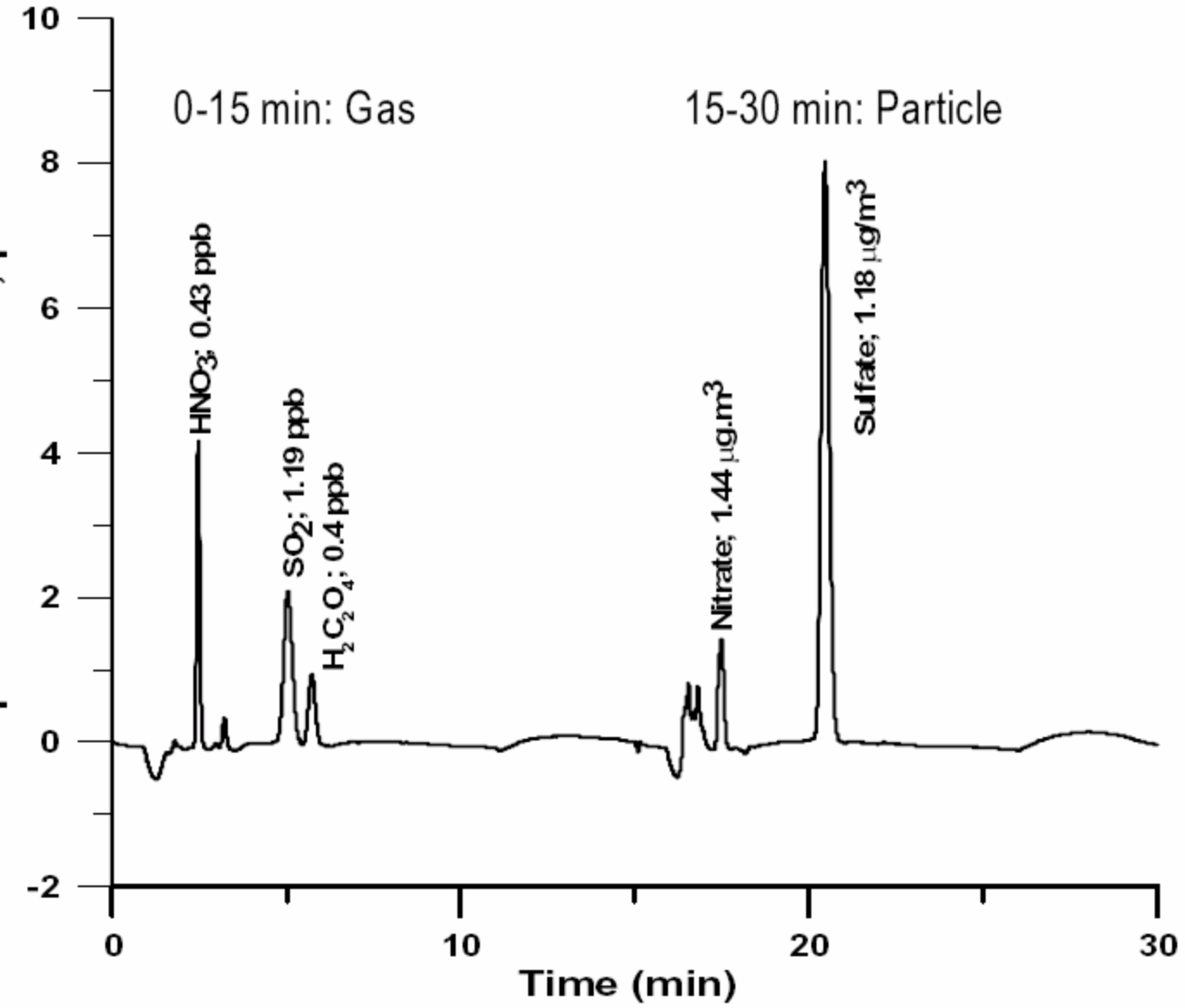
Membrane	Length cm	ID mm	Filament mm	Silicone Coating	% Removal 22 C	% Removal 30 C
Celgard	**50**	**0.4**	**0.2**	**Yes**	**91.5±0.3**	**96.6±0.6**
Celgard	**80**	**0.4**	**0.2**	**Yes**	**95.9±0.1**	**97.8±0.1**
Celgard	**100**	**0.4**	**0.2**	**Yes**	**97.7±0.2**	**99.4±0.2**
Neomecs	**50**	**0.2**	**No**	**PP**	**81.8±0.5**	**90.5±0.8**
Neomecs	**50**	**0.4**	**0.2**	**PP**	**91.5±0.1**	**92.9±0.2**

Lumen flow 1 mL/min; Sink solution: 100 mM NaOH at 0.5 mL/min


Without CO_2 Removal
Room Temperature CO_2 Removal
CO_2 Removal w in-line heater
When using a carbonate eluent (9 mM Na_2CO_3), 98% CO_2 is removed at room temperature
Oven at 30 – 35 C gives excellent results and low baseline noise
Separation on a TAC LP1 + AG 11 HC guard column
2 mM KOH eluent 1 mL/min
chloride, nitrate, carbonate, sulfate
Specific conductance, µS/cm
1.2
0.8
0.4
0
-0.4
0.0
4.0
8.0
12.0
16.0
Time, min

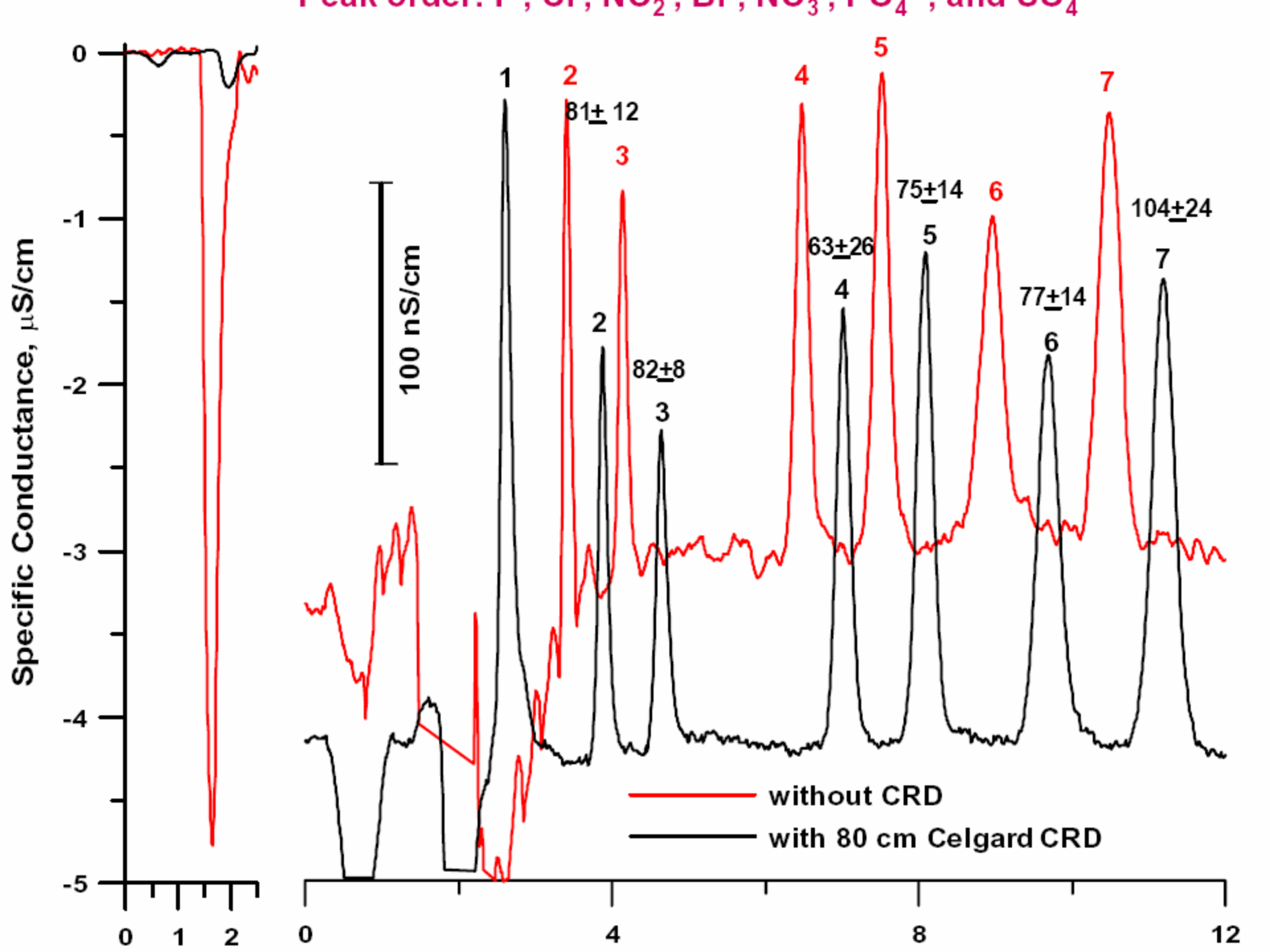

Ambient Measurements in Tampa, FL AG11/AS11 EG 40
(w/o d-CO2 device) 15.50 mM KOH, 1.50mL/min
vs.
(with) 17.50 mM KOH, 1.4 mL/min
Specific conductance, µS/cm
Specific conductance, µS/cm
Time, min
HCl
HONO
Carbonate
85ppt
40ppt
HNO3
SO2
H2C2O4
3
2
1
0
-1
8
6
4
2
0
-2
0.0
4.0
8.0
12.0
16.0

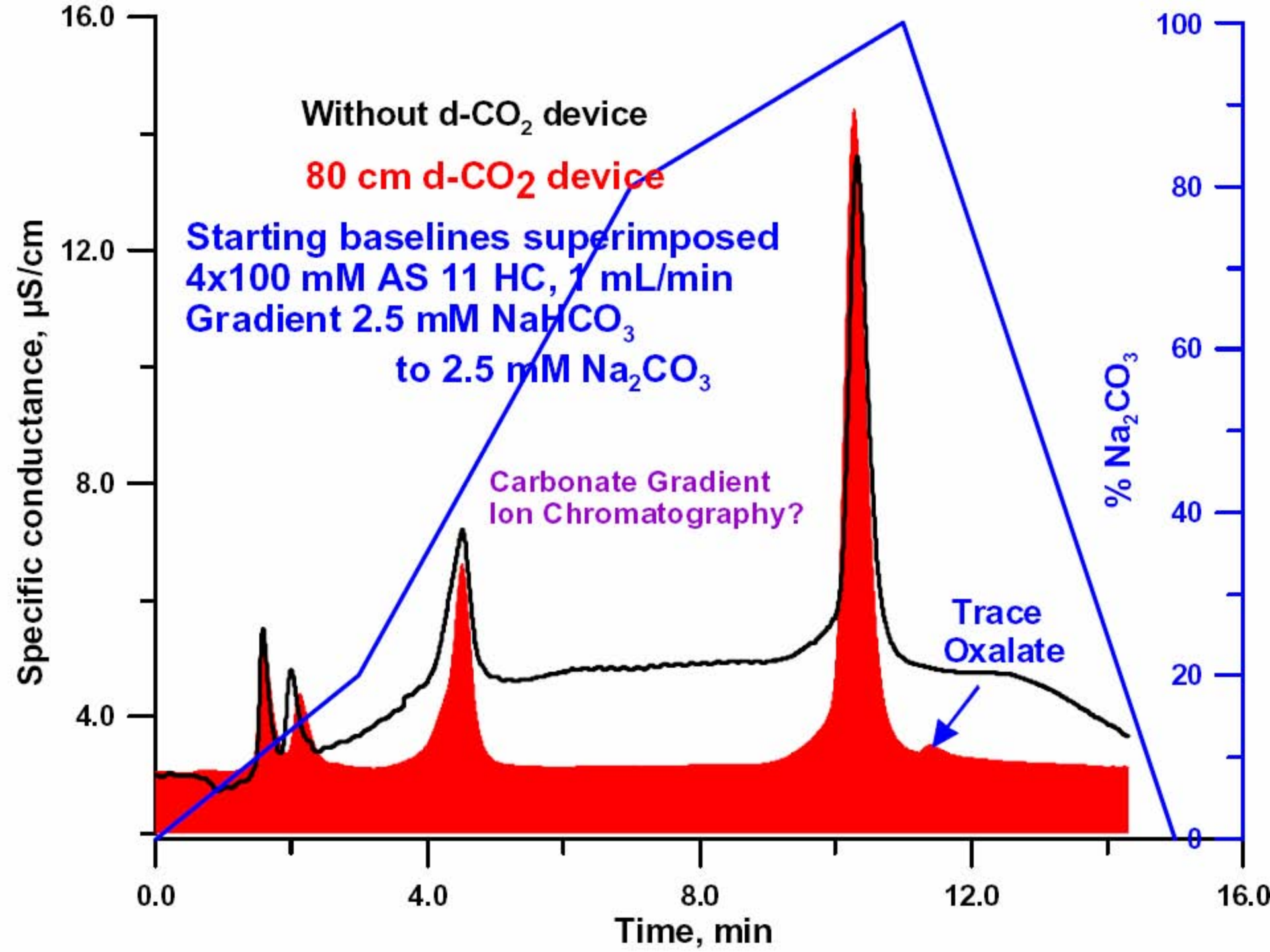
Gas Particle Ion Chromatography (GP-IC) System: Use of CRD in automated System to remove CO_2 from suppressed carbonate eluent



Automated sequentia chromatograms of collected gas and aerosol samples with 2.4 mM Na_2CO_3 and 2.3 mM $NaHCO_3$ eluent, 4X150 mm AG11 column, 1.0 mL/min, 80 cm Celgard CRD, oven a 30°C.

Background: From ~15µS to ≤1µS


Peak order: F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}
Specific Conductance, μS/cm
0
-1
-2
-3
-4
-5
0
1
2
0
4
8
12
100 nS/cm
1
2
81± 12
3
4
5
75±14
6
104±24
7
63±26
4
5
77±14
6
7
2
82±8
3
without CRD
with 80 cm Celgard CRD


Without d-CO2 device
80 cm d-CO2 device
Starting baselines superimposed
4x100 mM AS 11 HC, 1 mL/min
Gradient 2.5 mM NaHCO3
to 2.5 mM Na2CO3
Carbonate Gradient
Ion Chromatography?
Trace
Oxalate
Specific conductance, µS/cm
% Na2CO3
Time, min
16.0
12.0
8.0
4.0
0.0
4.0
8.0
12.0
16.0
100
80
60
40
20
0

CRD Unit

Our Version,

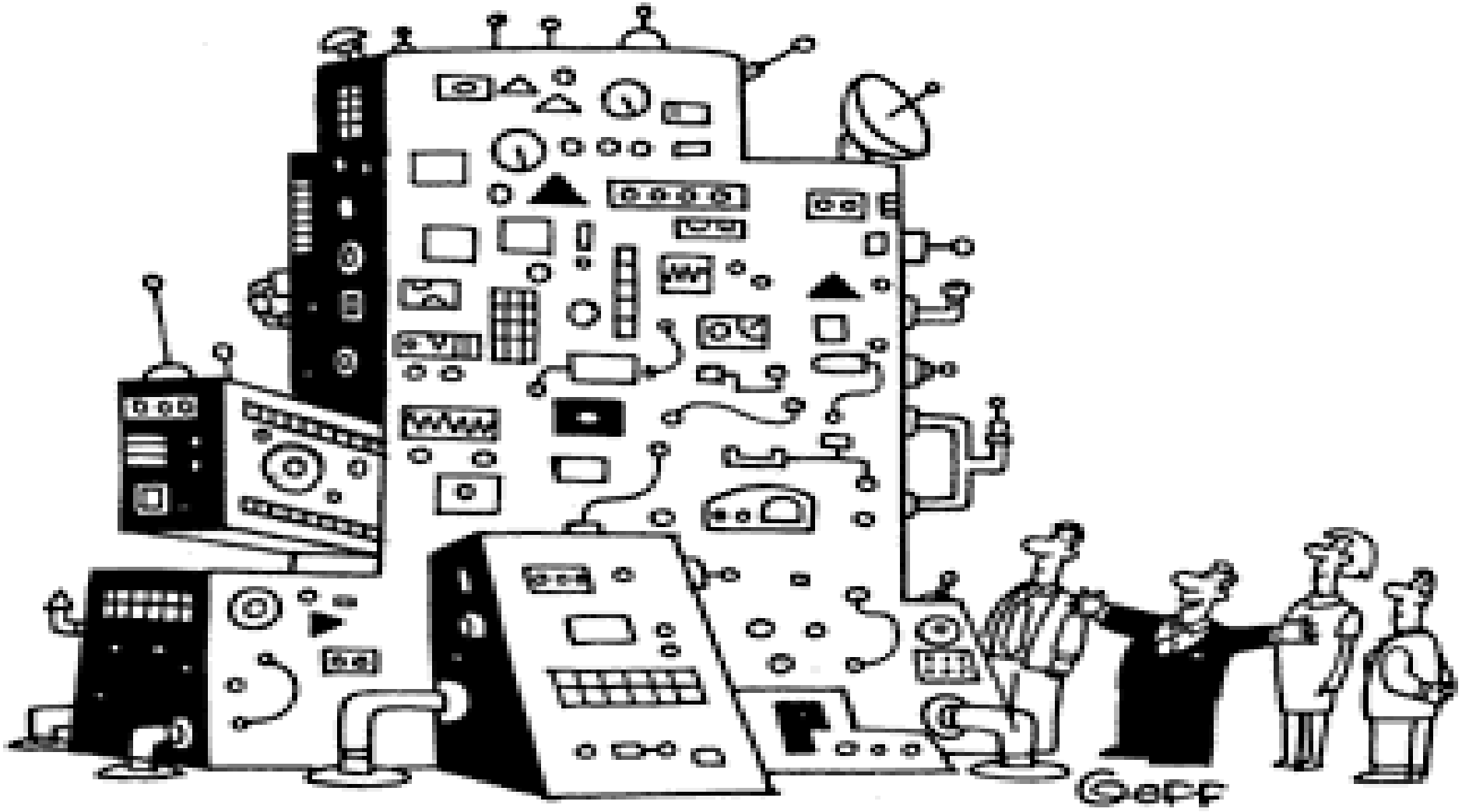
Asymmetric Membrane Fiber-Based Carbon Dioxide Removal Devices for Ion Chromatography
S. M. Rahmat Ullah, et al., DOI: 10.1021/ac0492160
Won Best Grduate Student Paper Award, ACS Division of Environmental Chemistry

This was commercialized. A patent was granted

Their Version

won a Pittcon Silver Award

And a IR-100 award

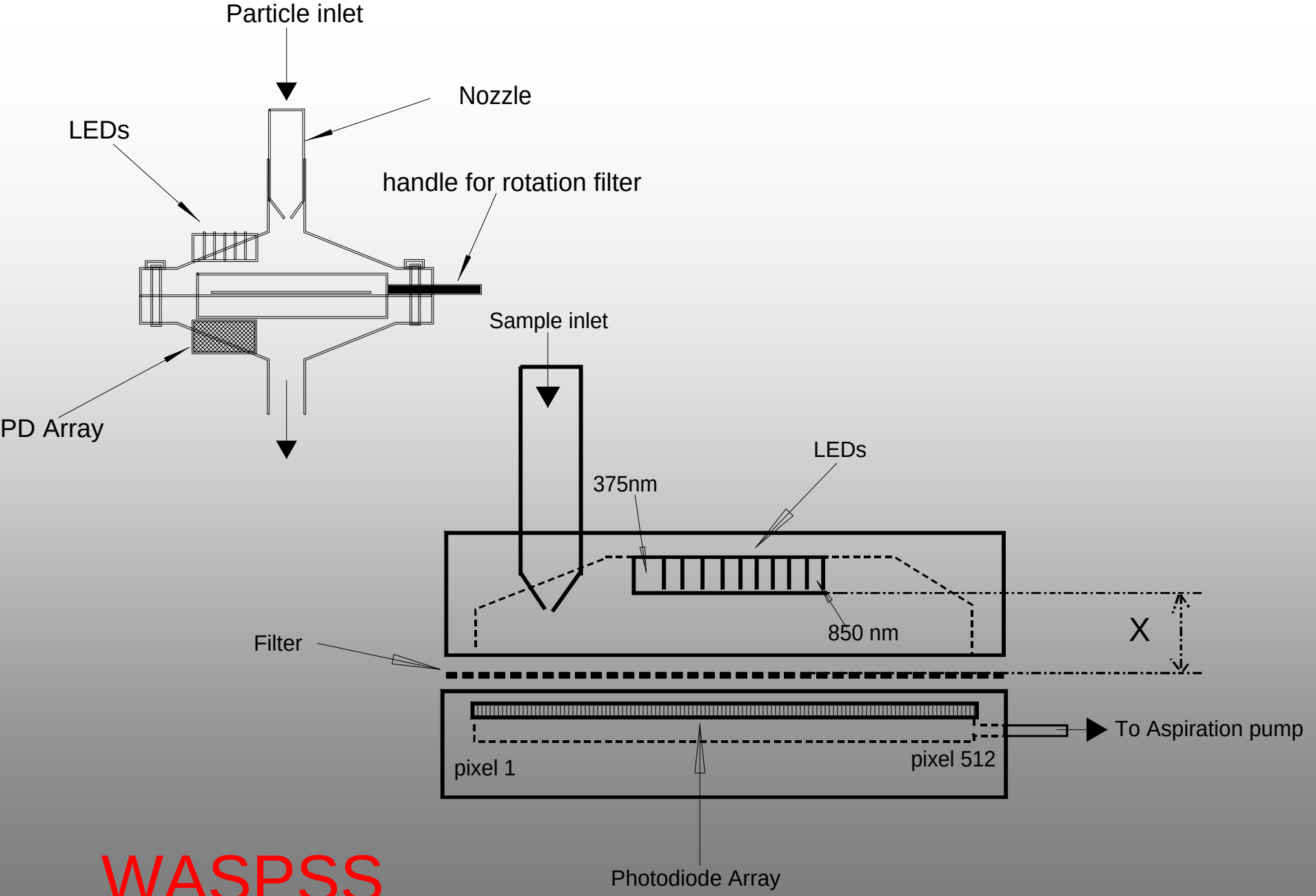


"Ladies and gentlemen, welcome to the future of the can opener!"

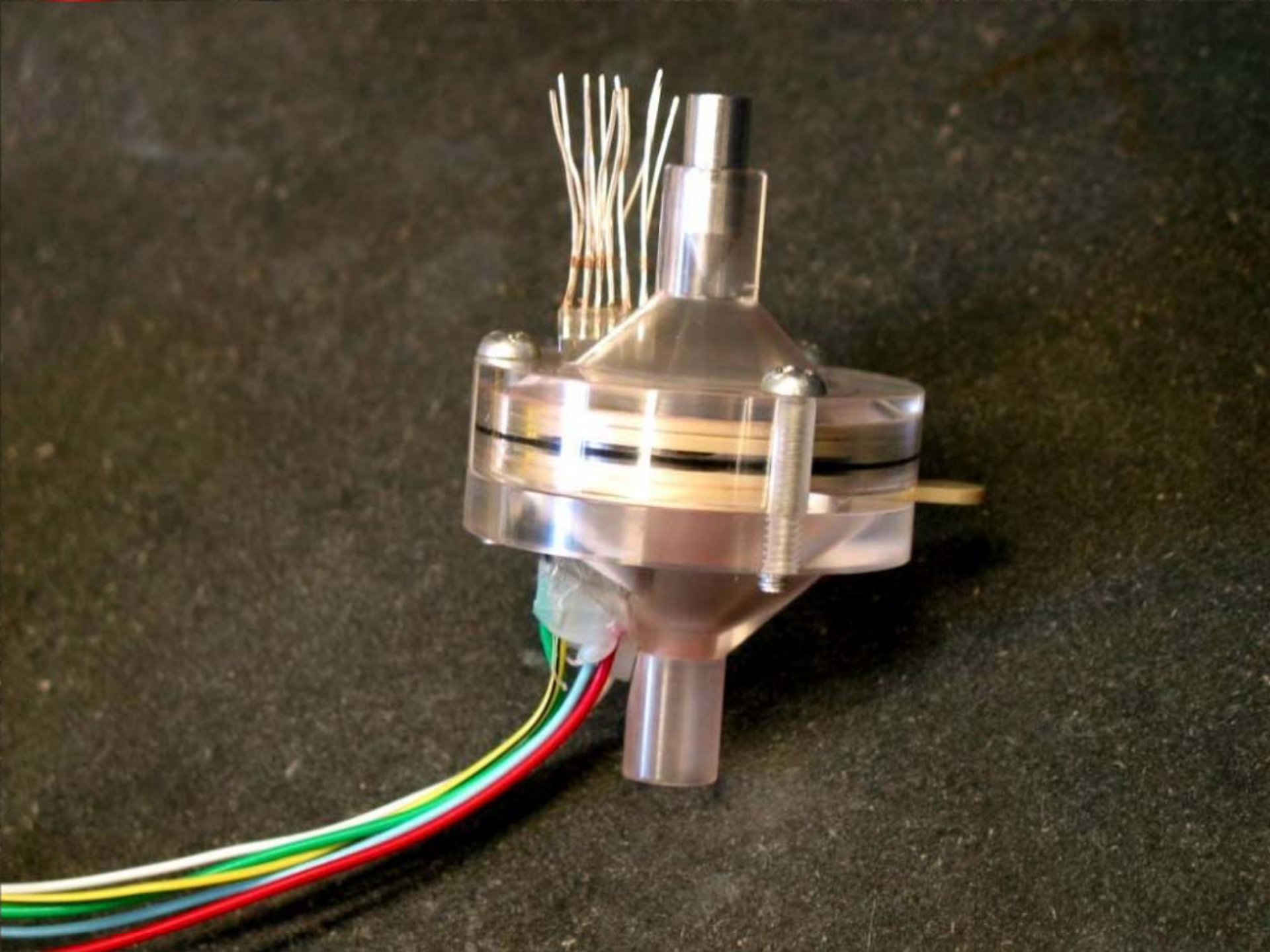
EPA STAR Project: EC OC LC - MS

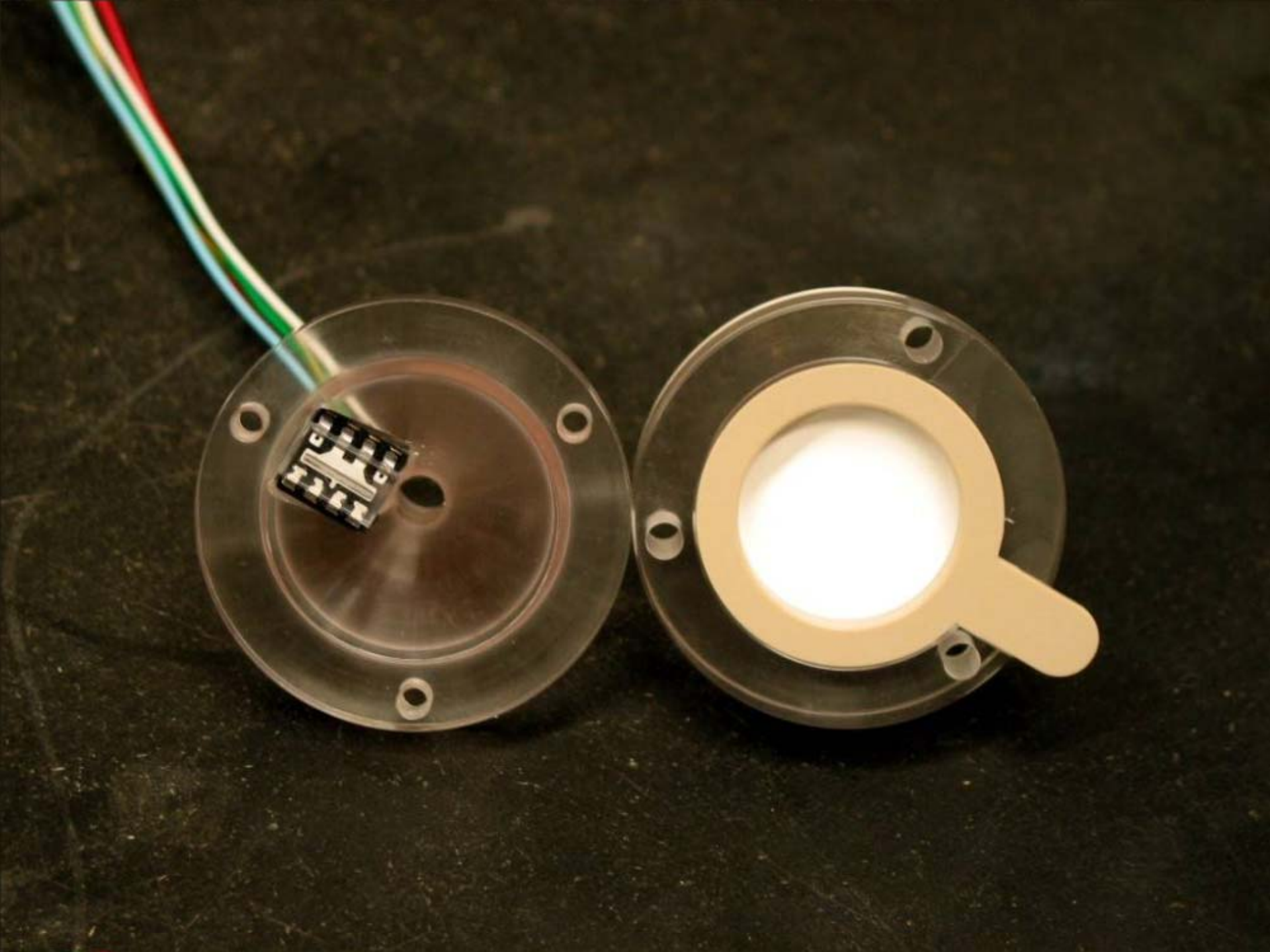
Wavelength-discriminating Aethalometric Size-Discriminating Particle Sensor (WASPS)

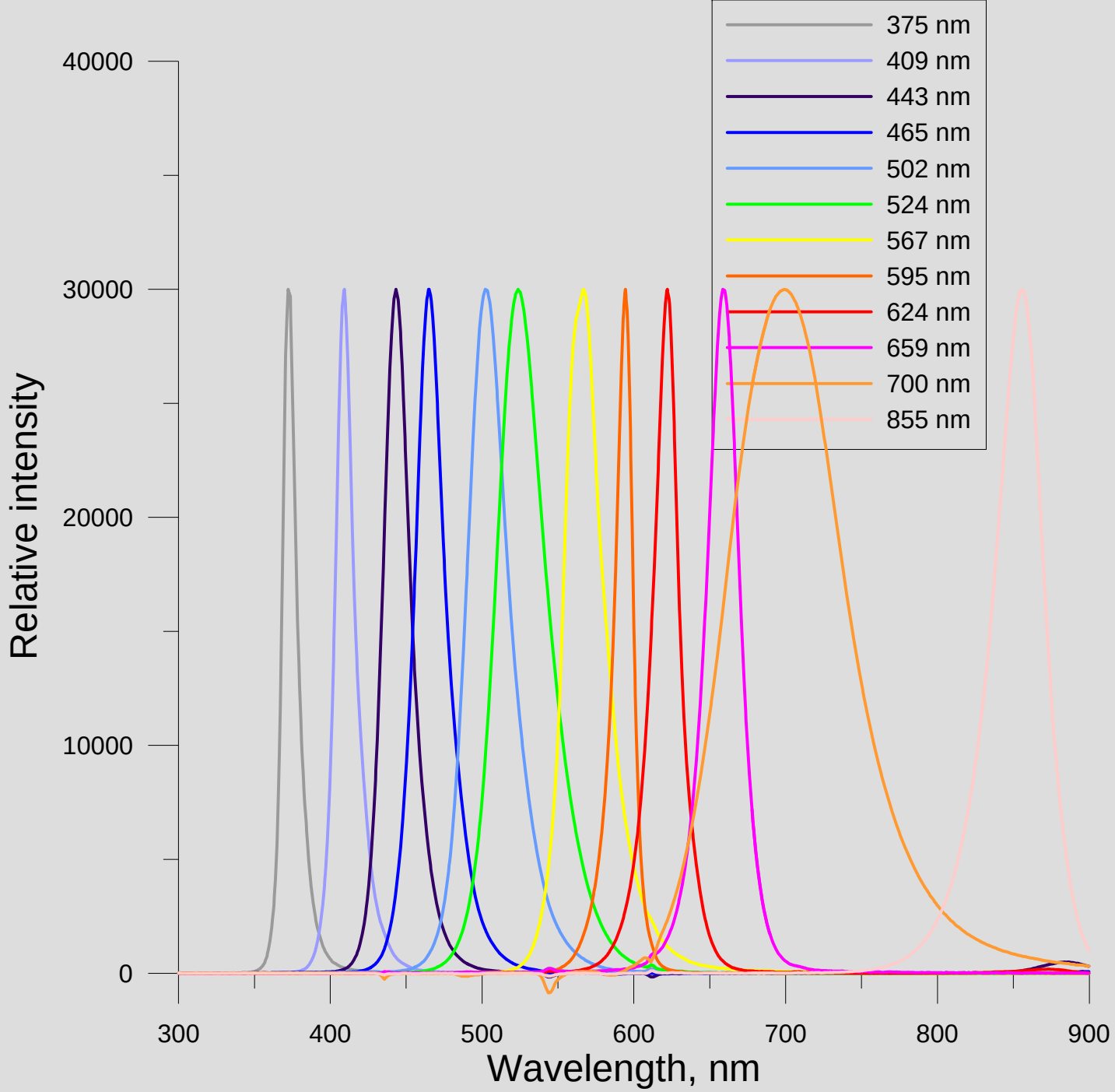
Excellent correlation of EC with low wavelength aethalometry


Particle inlet
Nozzle
LEDs
handle for rotation filter
Sample inlet
PD Array
LEDs
375nm
850 nm
X
Filter
To Aspiration pump
pixel 1
pixel 512
Photodiode Array

WASPSS





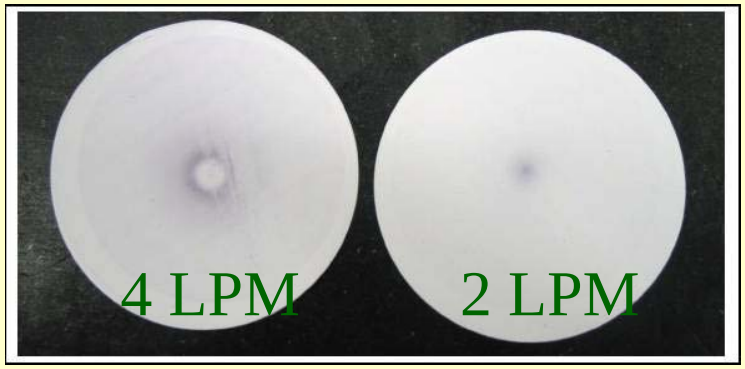

375 nm
409 nm
443 nm
465 nm
502 nm
524 nm
567 nm
595 nm
624 nm
659 nm
700 nm
855 nm
40000
30000
20000
10000
0
Relative intensity
300
400
500
600
700
800
900
Wavelength, nm

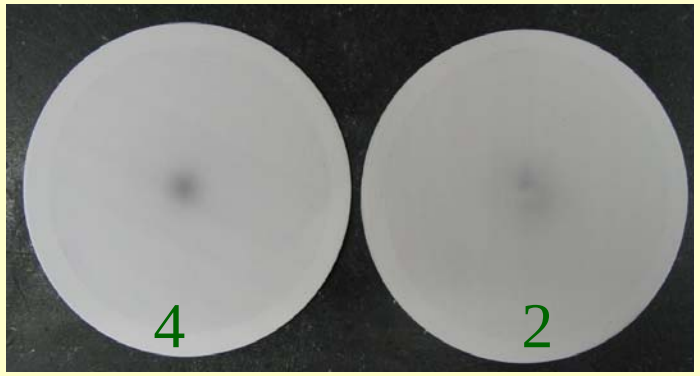
Factors affecting particle distribution patterns

- **Particle inlet tube size**
- **Sampling flow rate**
- **Distance between Nozzle and filter**
- **Particle size**

Air velocity at the nozzle 0.5 μm MMAD particles

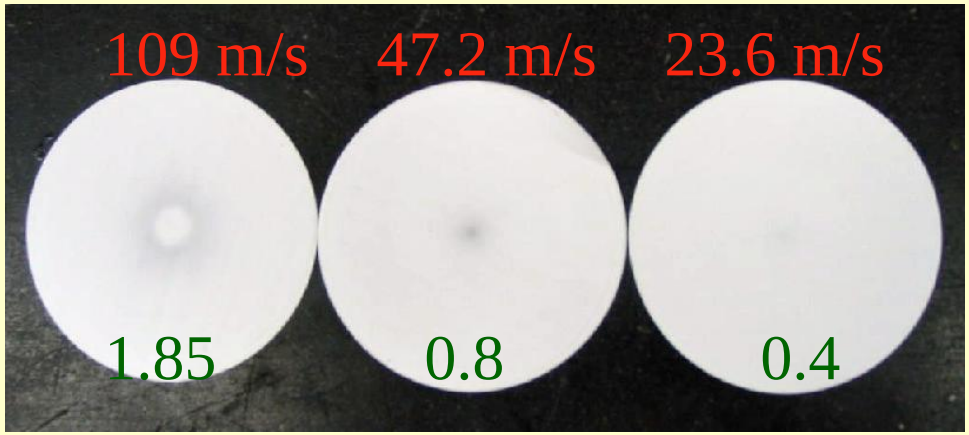
1.2 mm noz





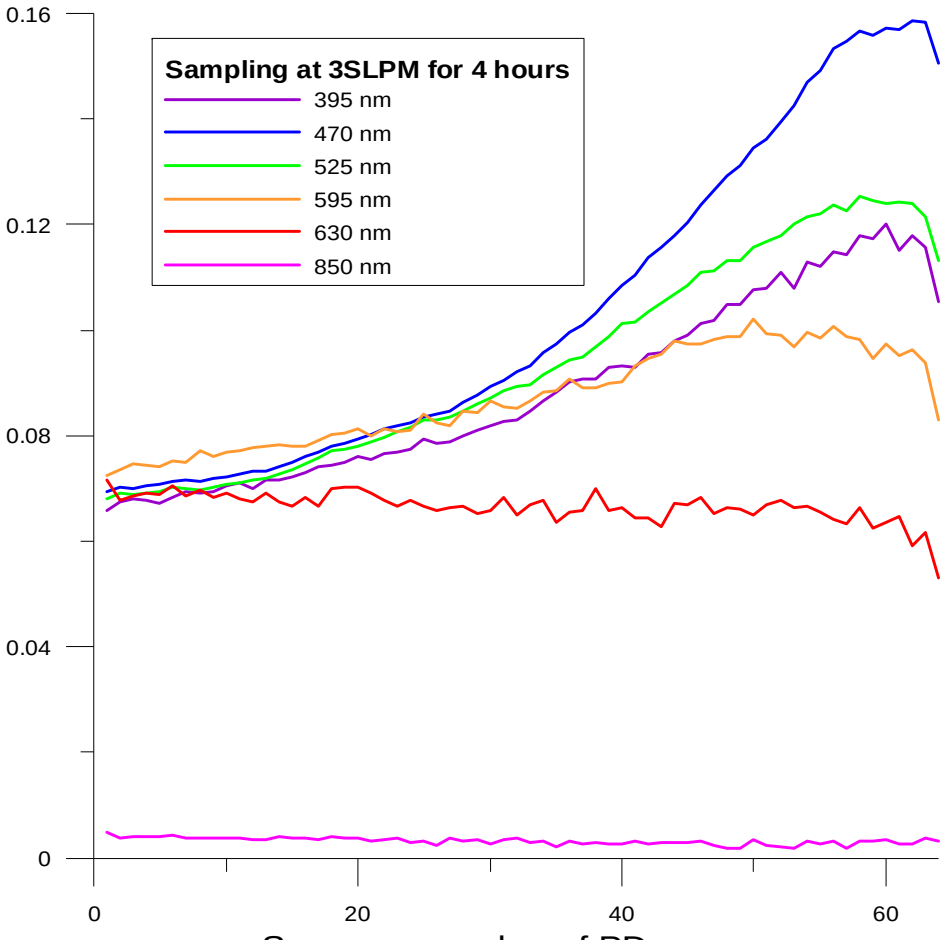
1.9 mm

0.5 mm



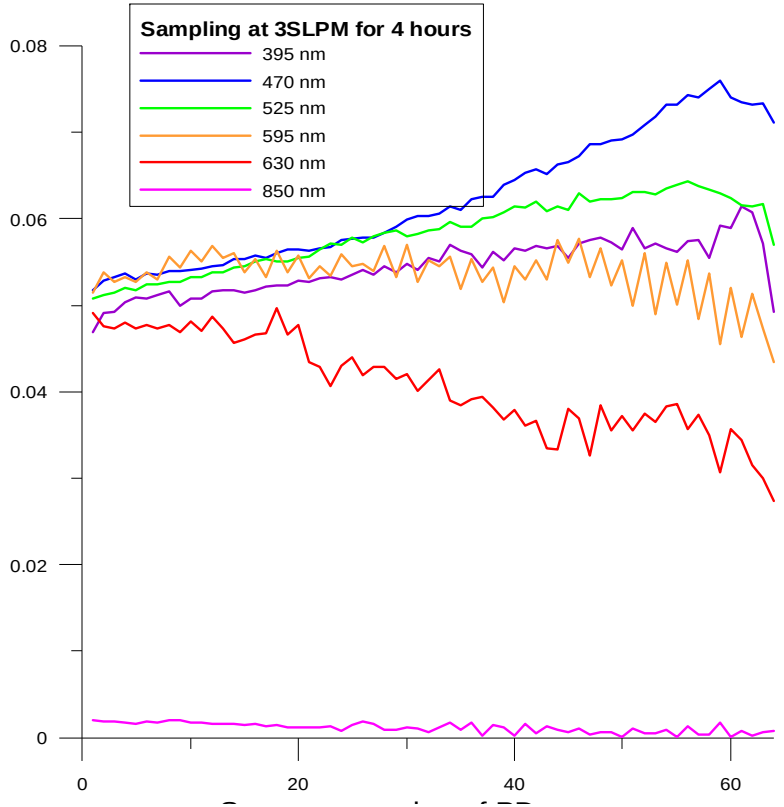
For 0.5 μm particles, Nozzle velocity should be controlled between 10 to 50 m/s

Big particle distribution

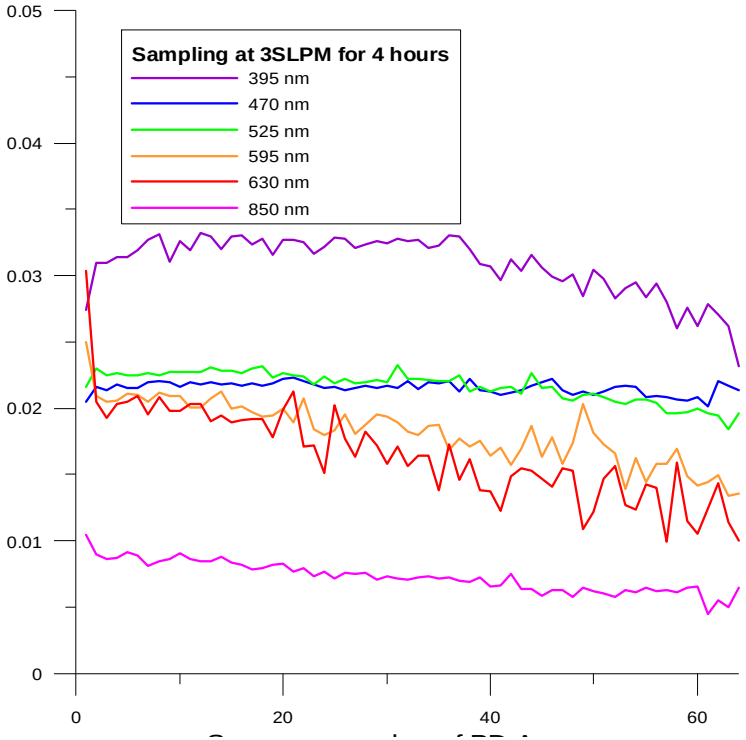


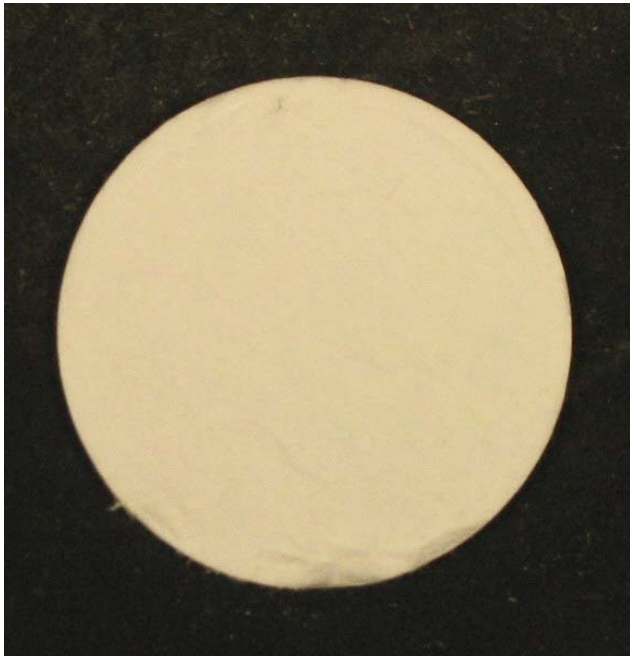
Medium Particle distribution

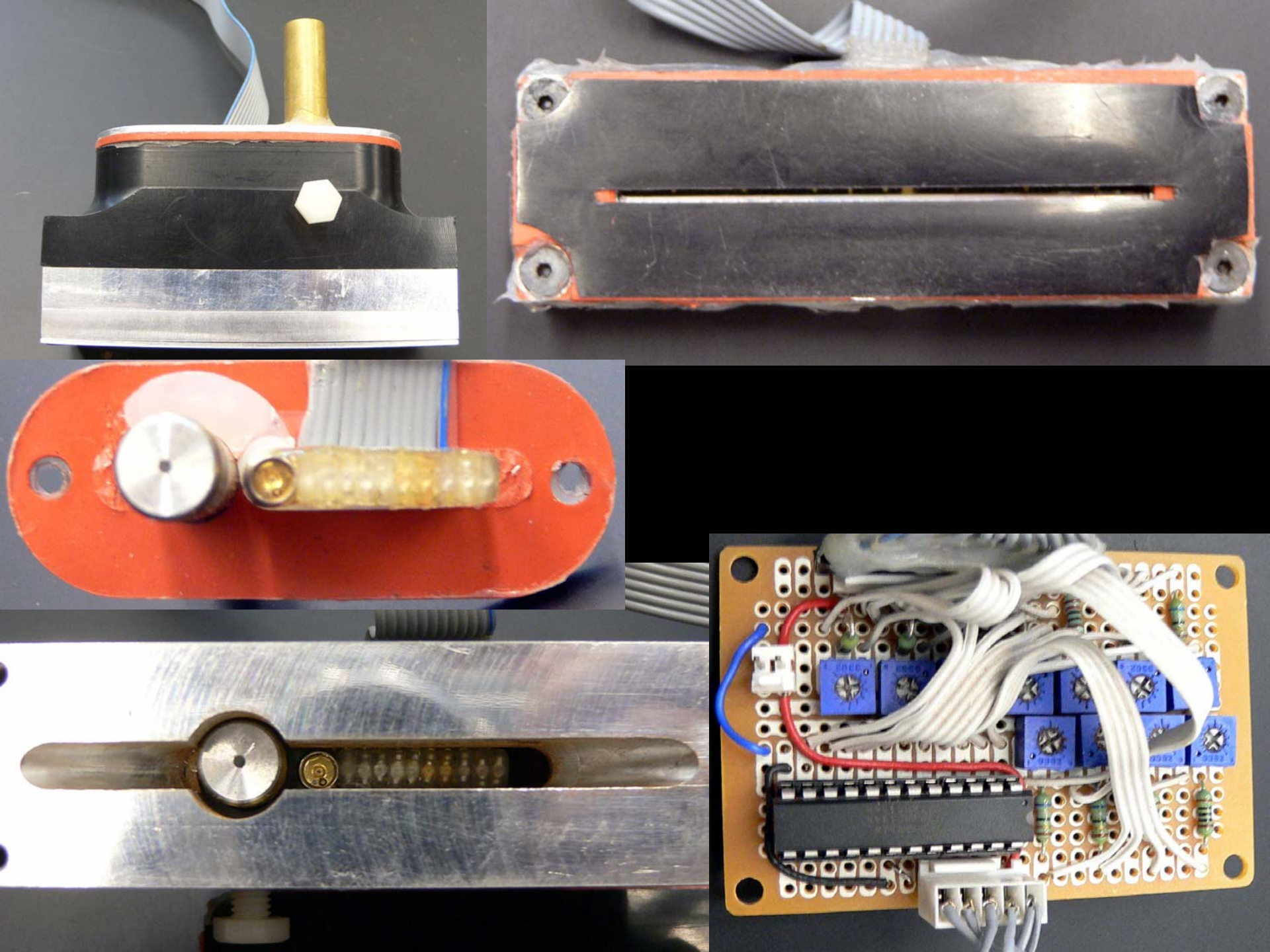
0.1-0.2 μm	0.2-0.3μm	0.3-0.5 μm	0.5-1.0 μm	1.0-3.0 μm	>3 μm
31	16	11061	376	2	2

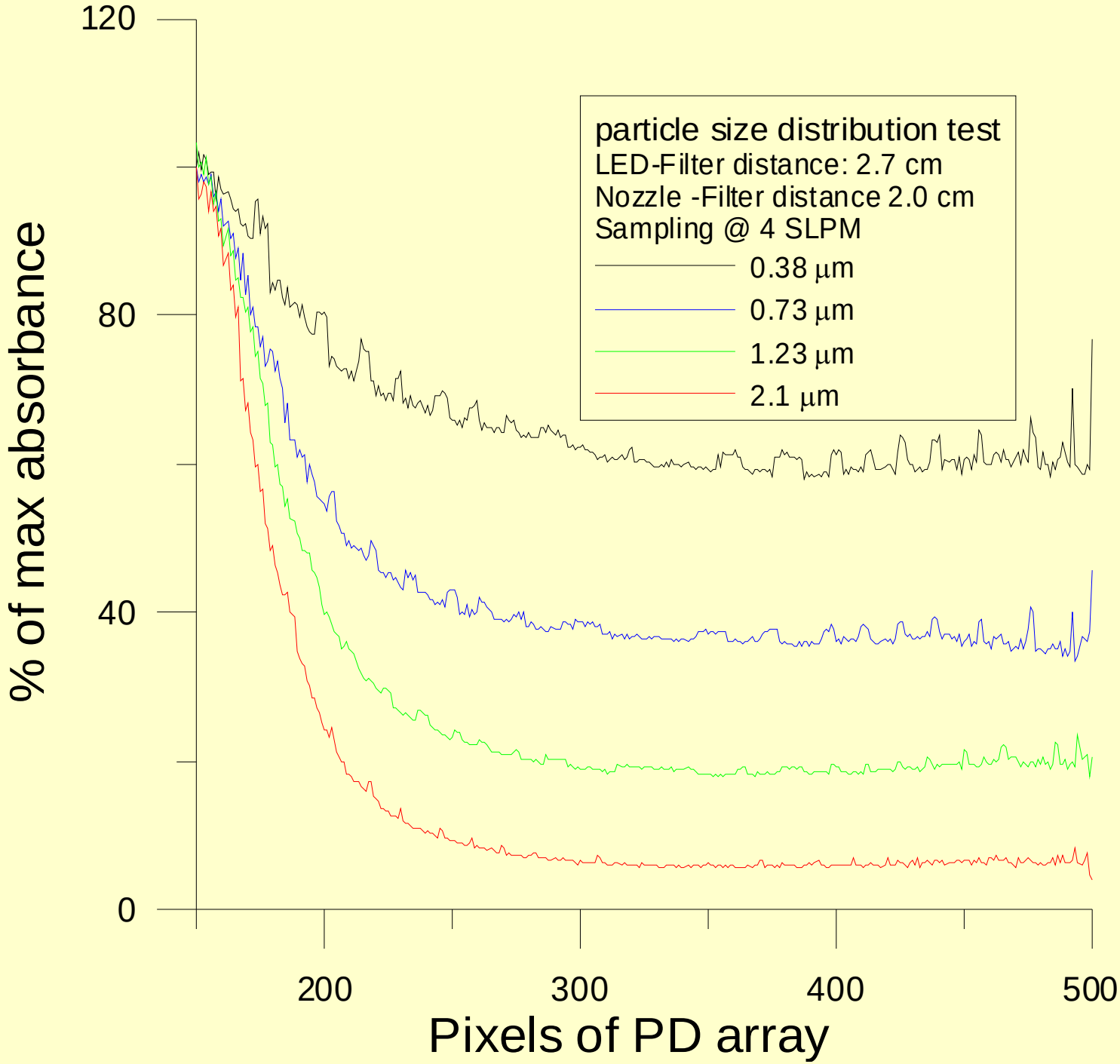


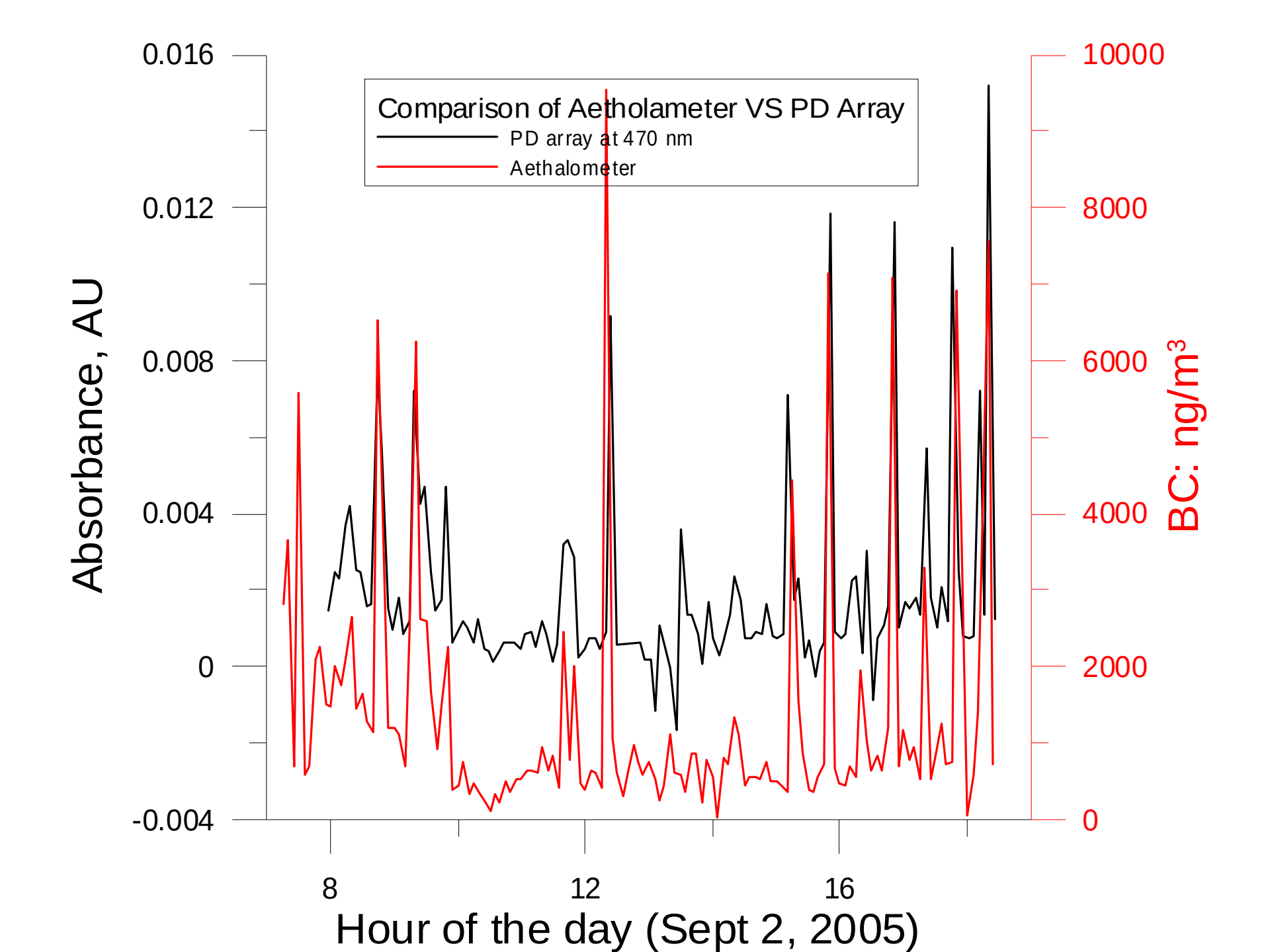
Small Particle distribution

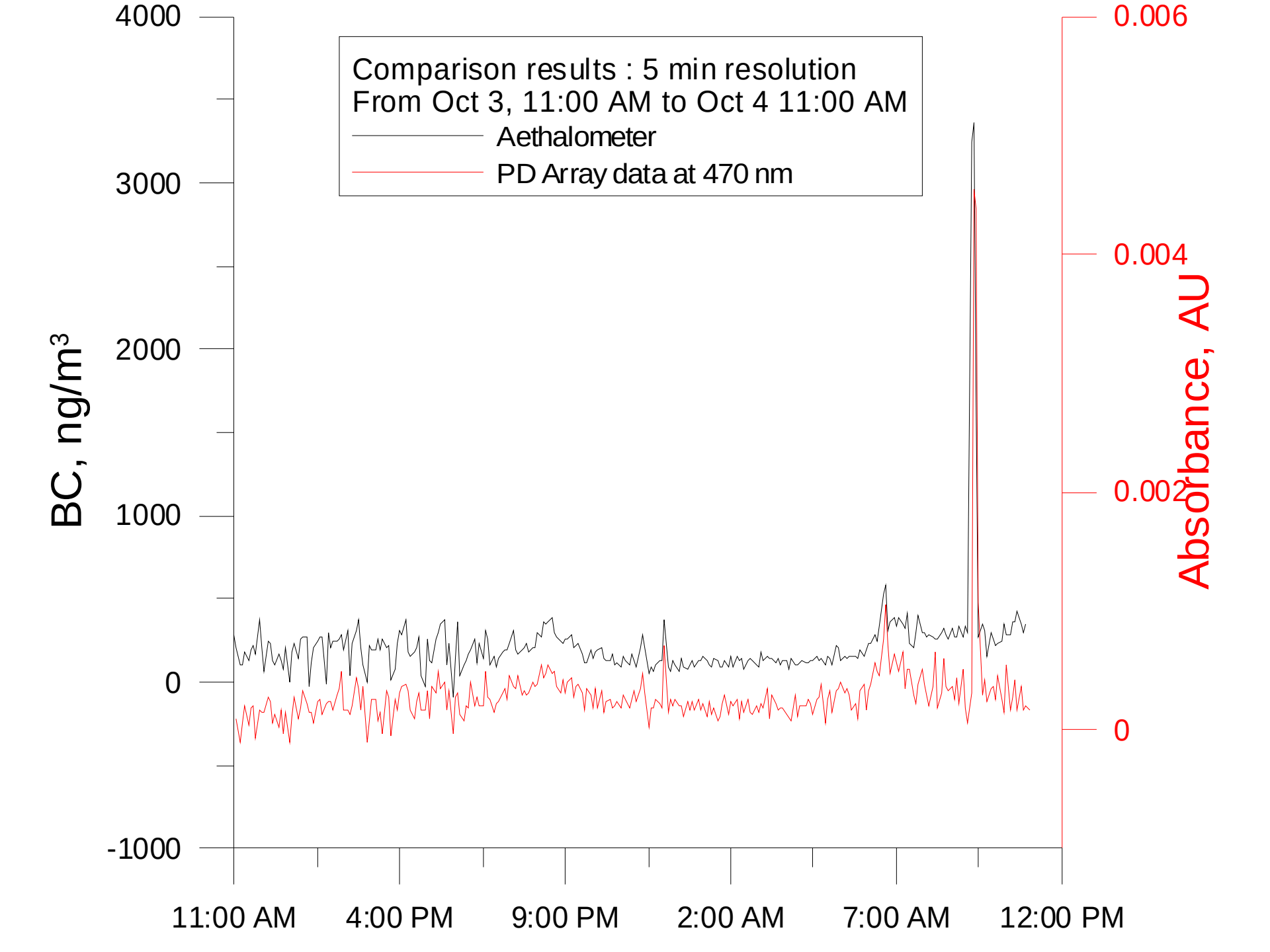


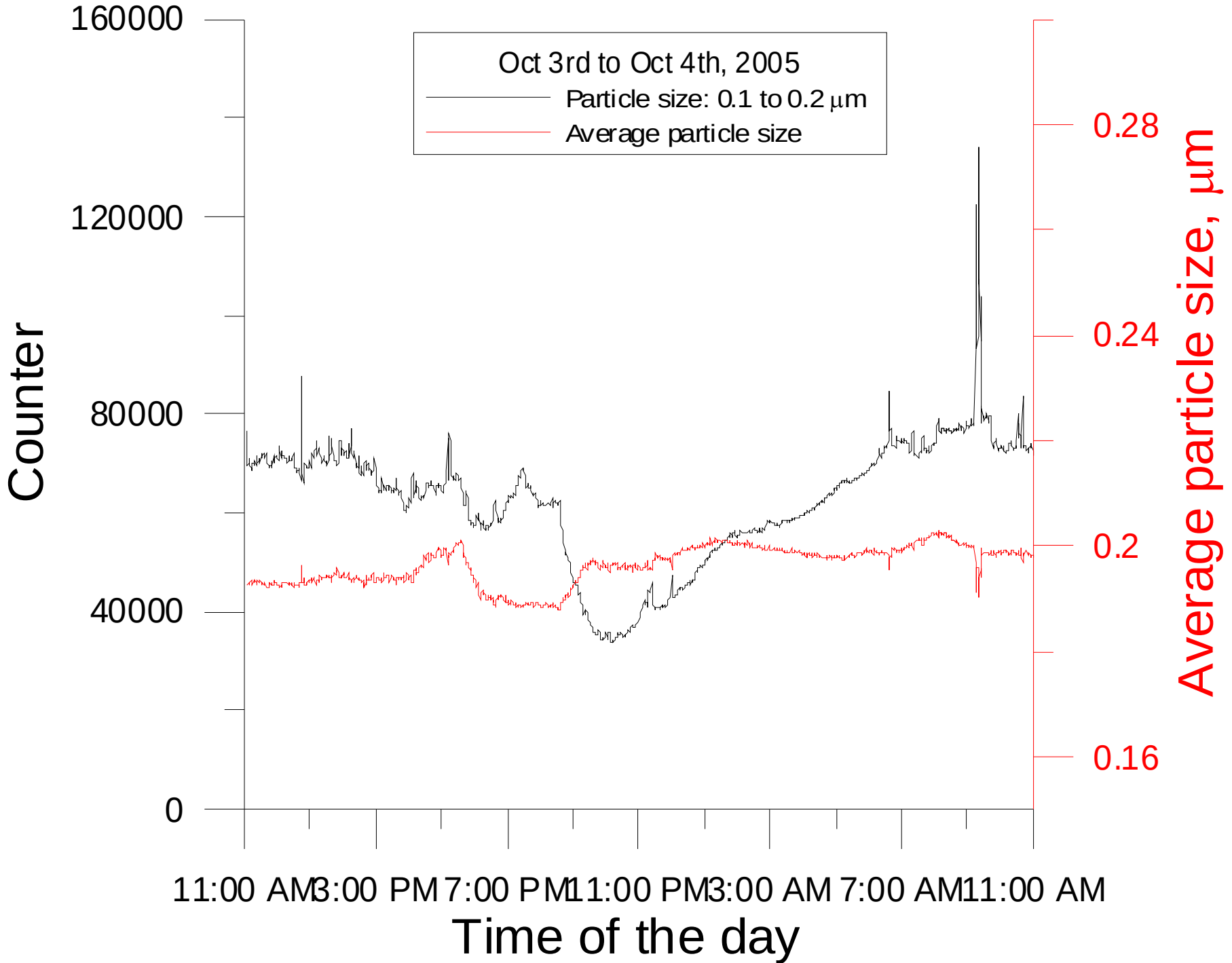


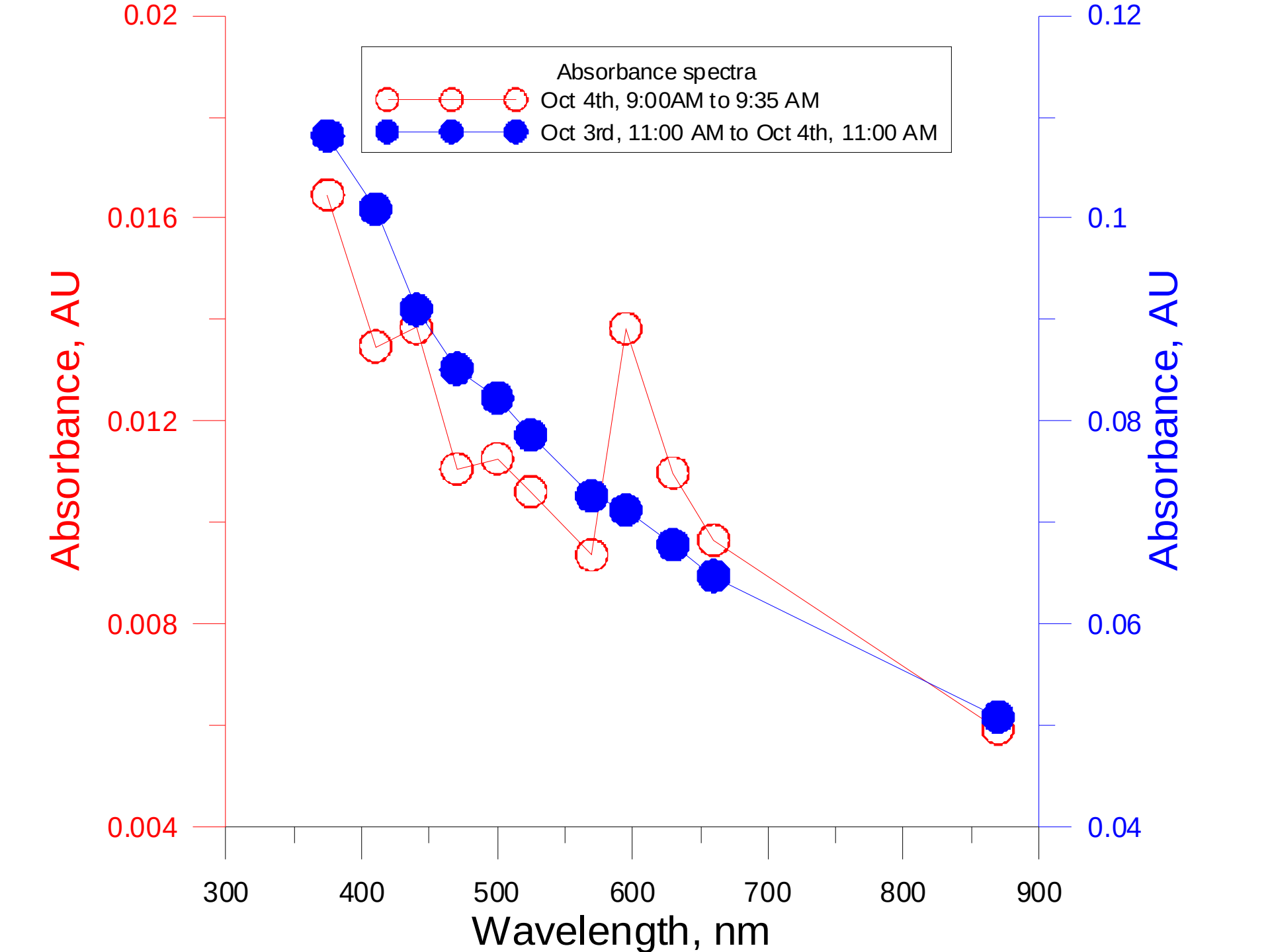


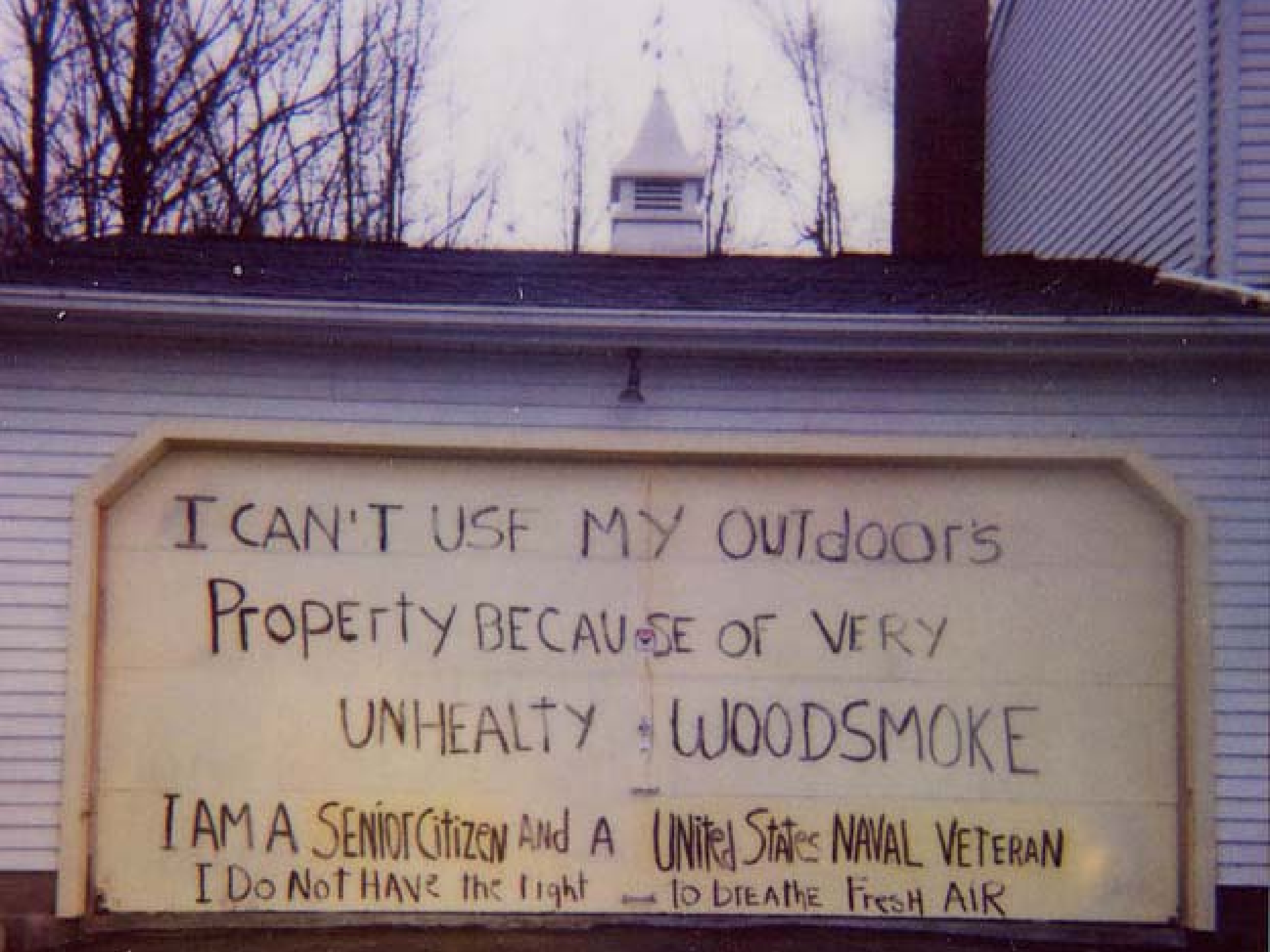

particle size distribution test
LED-Filter distance: 2.7 cm
Nozzle -Filter distance 2.0 cm
Sampling @ 4 SLPM
0.38 μm
0.73 μm
1.23 μm
2.1 μm
% of max absorbance
120
80
40
0
200
300
400
500
Pixels of PD array

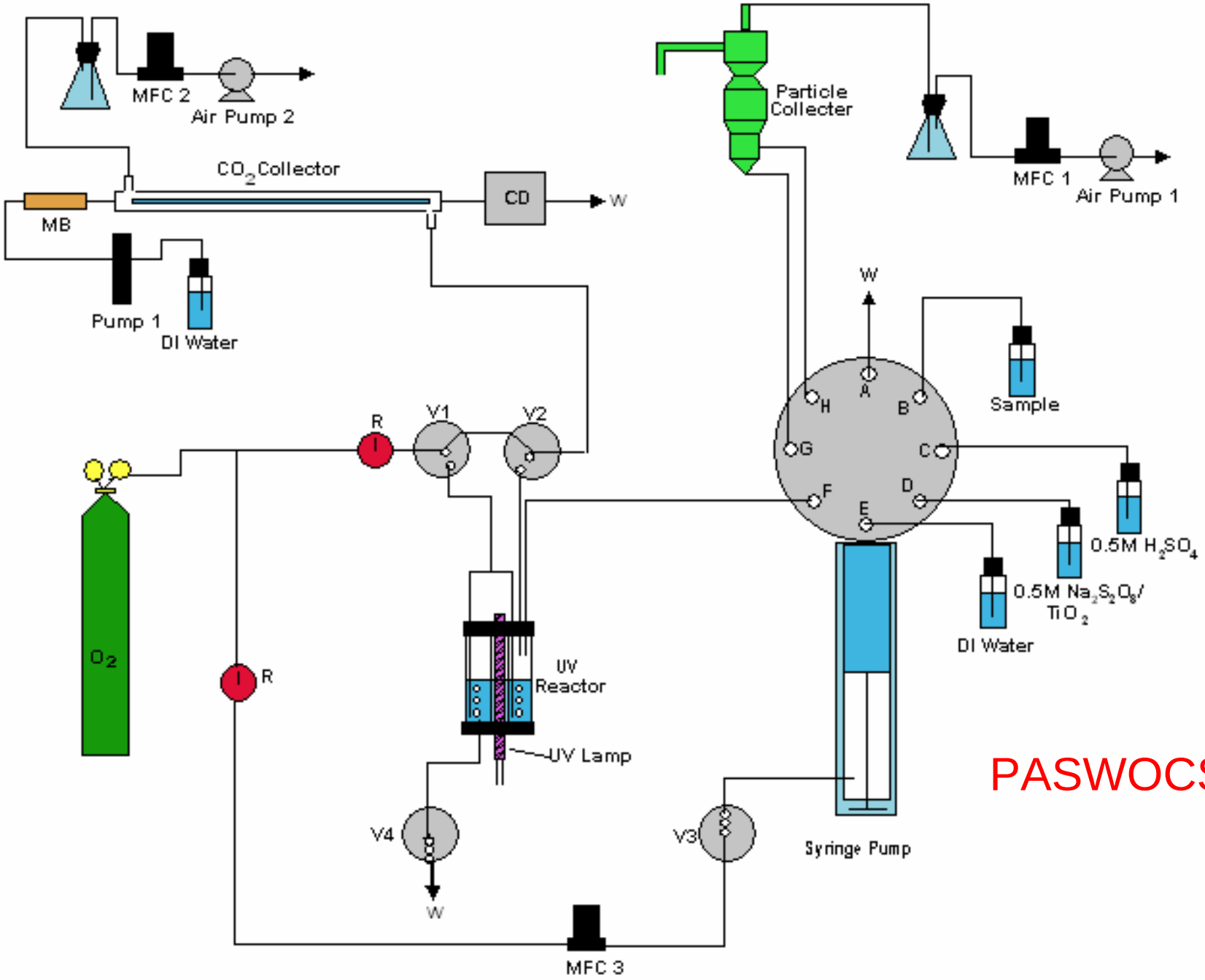

Comparison of Aetholameter VS PD Array
PD array at 470 nm
Aethalometer
Absorbance, AU
BC: ng/m³
0.016
0.012
0.008
0.004
0
-0.004
10000
8000
6000
4000
2000
0
8
12
16
Hour of the day (Sept 2, 2005)

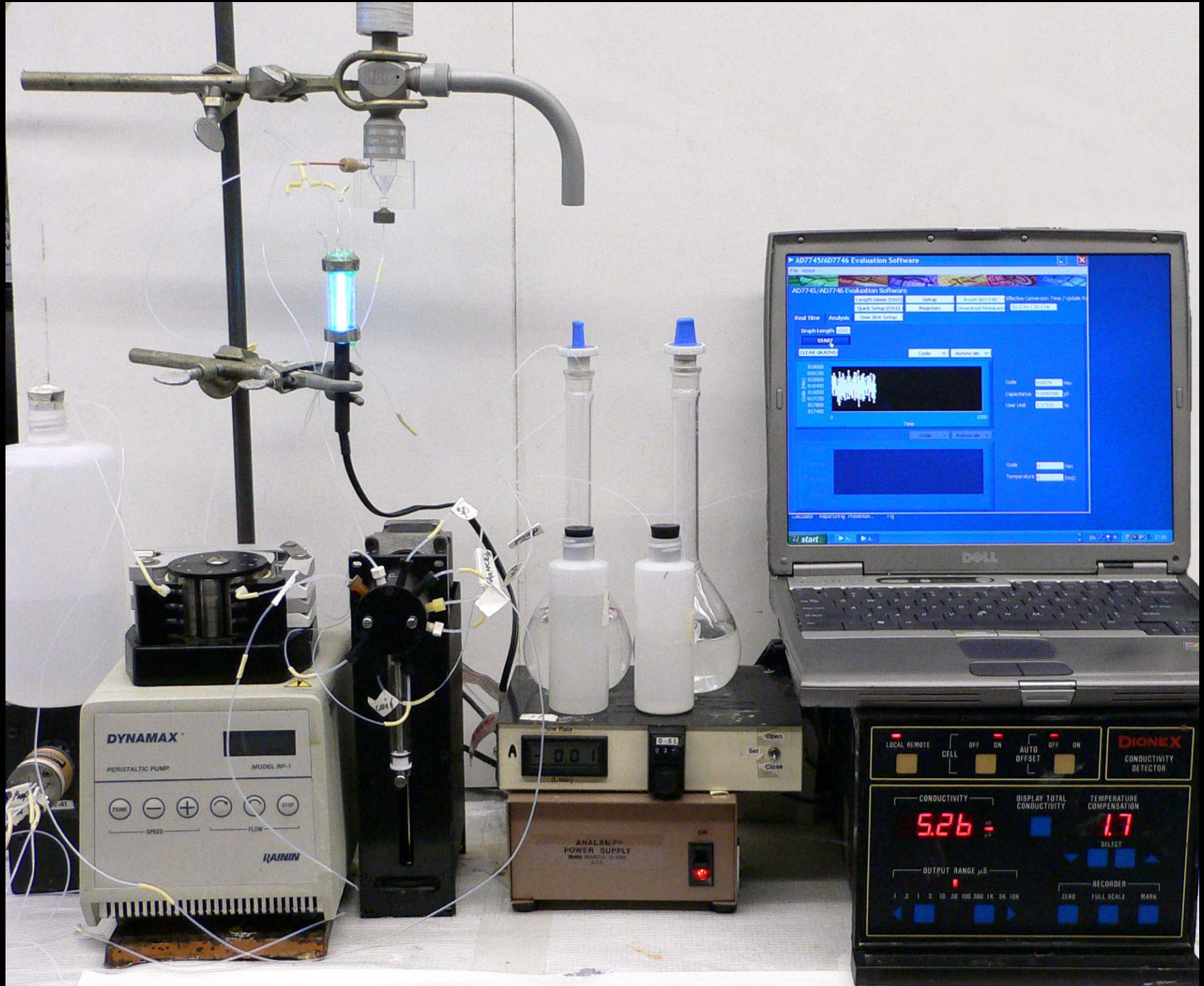

Comparison results : 5 min resolution
From Oct 3, 11:00 AM to Oct 4 11:00 AM
Aethalometer
PD Array data at 470 nm
BC, ng/m3
Absorbance, AU
4000
3000
2000
1000
0
-1000
0.006
0.004
0.002
0
11:00 AM
4:00 PM
9:00 PM
2:00 AM
7:00 AM
12:00 PM

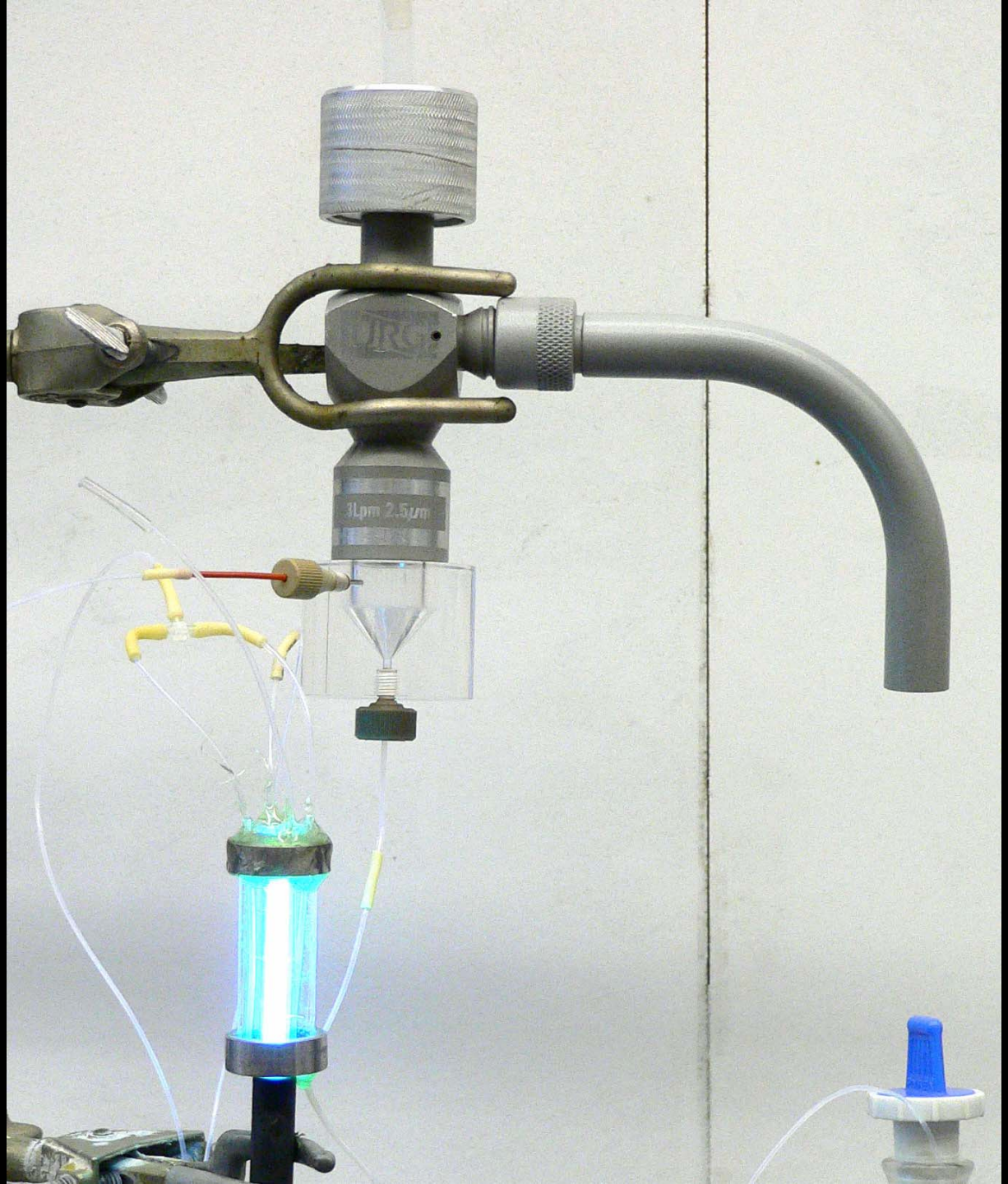

Oct 3rd to Oct 4th, 2005
Particle size: 0.1 to 0.2 μm
Average particle size
160000
120000
80000
40000
0
Counter
0.28
0.24
0.2
0.16
Average particle size, μm
11:00 AM
3:00 PM
7:00 PM
11:00 PM
3:00 AM
7:00 AM
11:00 AM
Time of the day

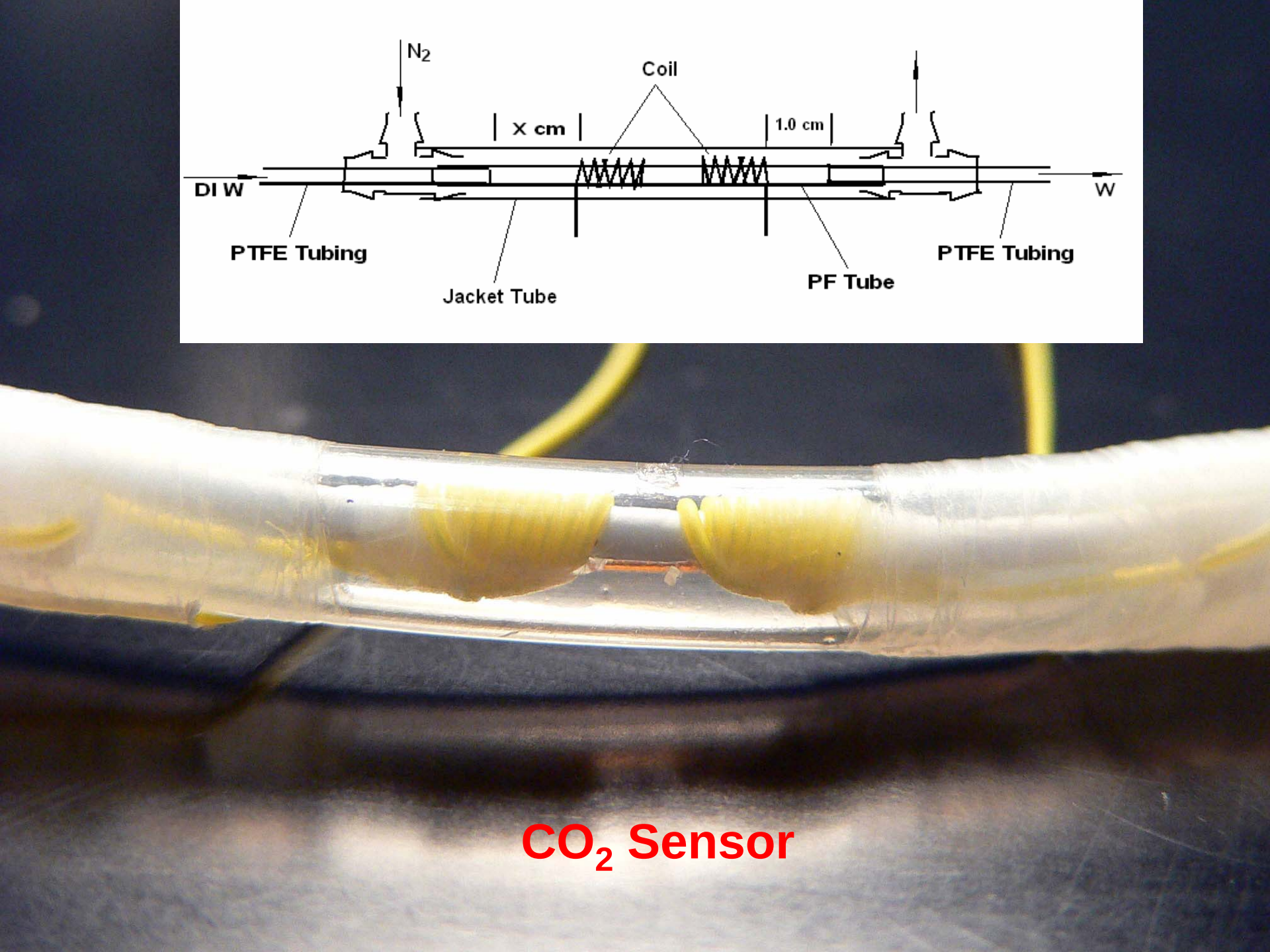

Absorbance spectra
Oct 4th, 9:00AM to 9:35 AM
Oct 3rd, 11:00 AM to Oct 4th, 11:00 AM
Absorbance, AU
0.02
0.016
0.012
0.008
0.004
0.12
0.1
0.08
0.06
0.04
300
400
500
600
700
800
900
Wavelength, nm


I CAN'T USE MY OUTdoor's
Property BECAUSE OF VERY
UNHEALTY WOODSMOKE
I AM A SENIOR Citizen And A United States NAVAL VETERAN
I Do Not HAVE the right to BREATHE Fresh AIR


MFC 2
Air Pump 2
CO_2 Collector
MB
CD
W
Pump 1
DI Water
Particle Collecter
MFC 1
Air Pump 1
W
Sample
R
V1
V2
A
B
C
D
E
F
G
H
O_2
R
UV Reactor
UV Lamp
0.5M H_2SO_4
0.5M $Na_2S_2O_8$/ TiO_2
DI Water
V4
V3
W
Syringe Pump
MFC 3
PASWOCS


AD7745/AD7746 Evaluation Software
DYNAMAX
PERISTALTIC PUMP
MODEL RP-1
RAININ
ANALAB PP-
POWER SUPPLY
DIONEX
CONDUCTIVITY DETECTOR
LOCAL REMOTE
CELL
AUTO OFFSET
CONDUCTIVITY
DISPLAY TOTAL CONDUCTIVITY
TEMPERATURE COMPENSATION
5.26
1.7
OUTPUT RANGE µS
RECORDER
ZERO
FULL SCALE
MARK
DELL


3Lpm 2.5µm


N_2
Coil
X cm
1.0 cm
DI W
W
PTFE Tubing
Jacket Tube
PF Tube
PTFE Tubing
CO_2 Sensor


ANALOG DEVICES
AD7745/46 EVALUATION BOARD
WITH CAPACITIVE LENGTH SENSOR DEMO
EVAL-AD7745/46EB
ANALOG DEVICES
E246366
Rev. A3

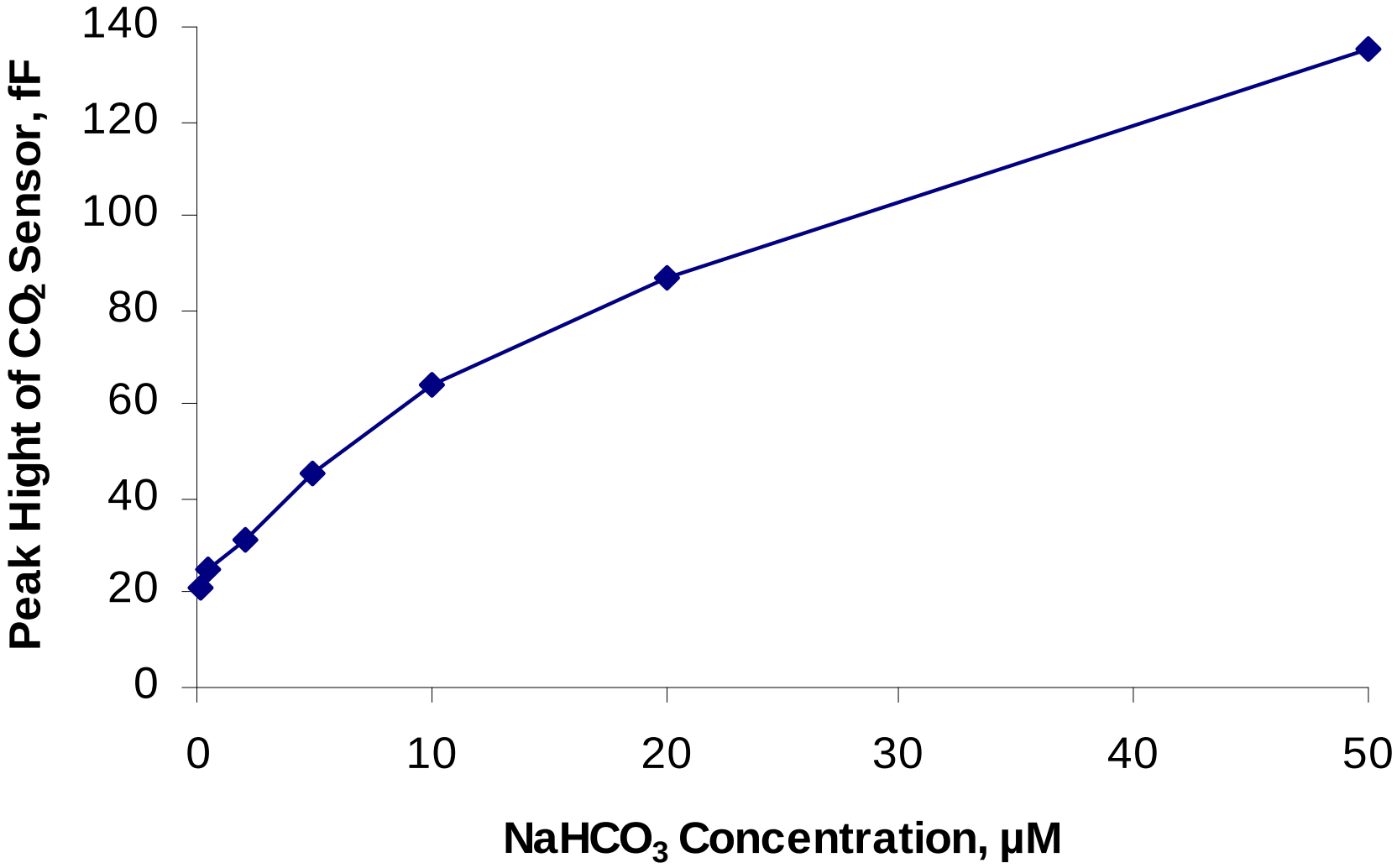
Absorber Considerations for CO_2 Sensor

DI water:

Low background; positive peak; easy to purify; no reagent; not linear.

LiOH Solution:

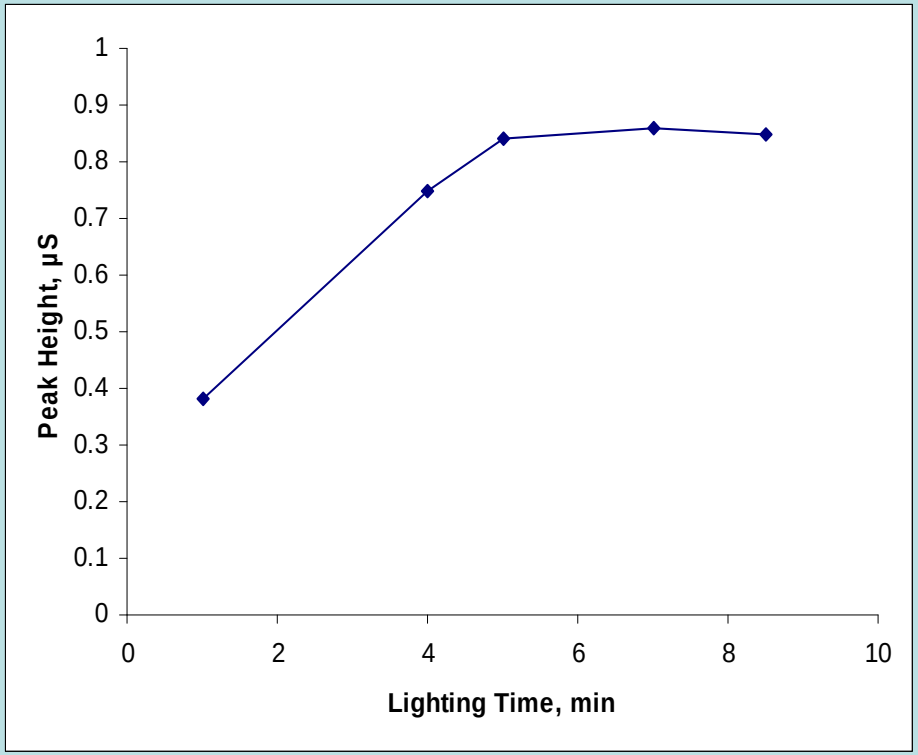
Linear to response; better absorbance; negative peak; high background.


Peak Hight of CO_2 Sensor, fF
140
120
100
80
60
40
20
0
0
10
20
30
40
50
$NaHCO_3$ Concentration, μM

Methods for Degradation

- **Acidification and initial measurement of inorganic carbonate carbon**
- **UV Light**
- **TiO_2 (Catalyst)**
- **$Na_2S_2O_8$/Other Oxidations**

Influence of UV Lighting Time for Glucose Decomposition

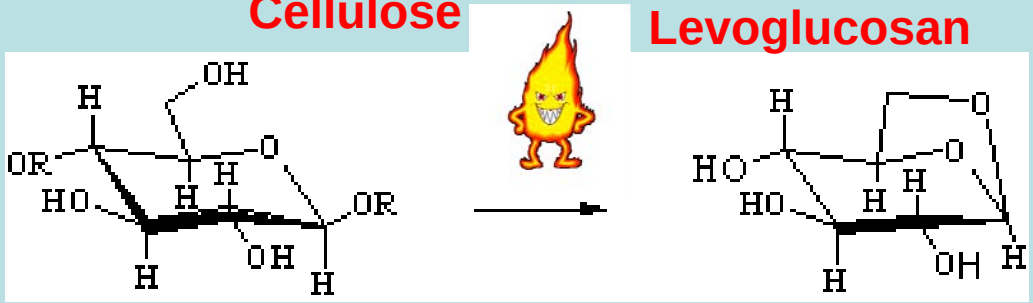


Glucose and most other simple sugars can be completely oxi-dized in 5 min using just UV light.

➔

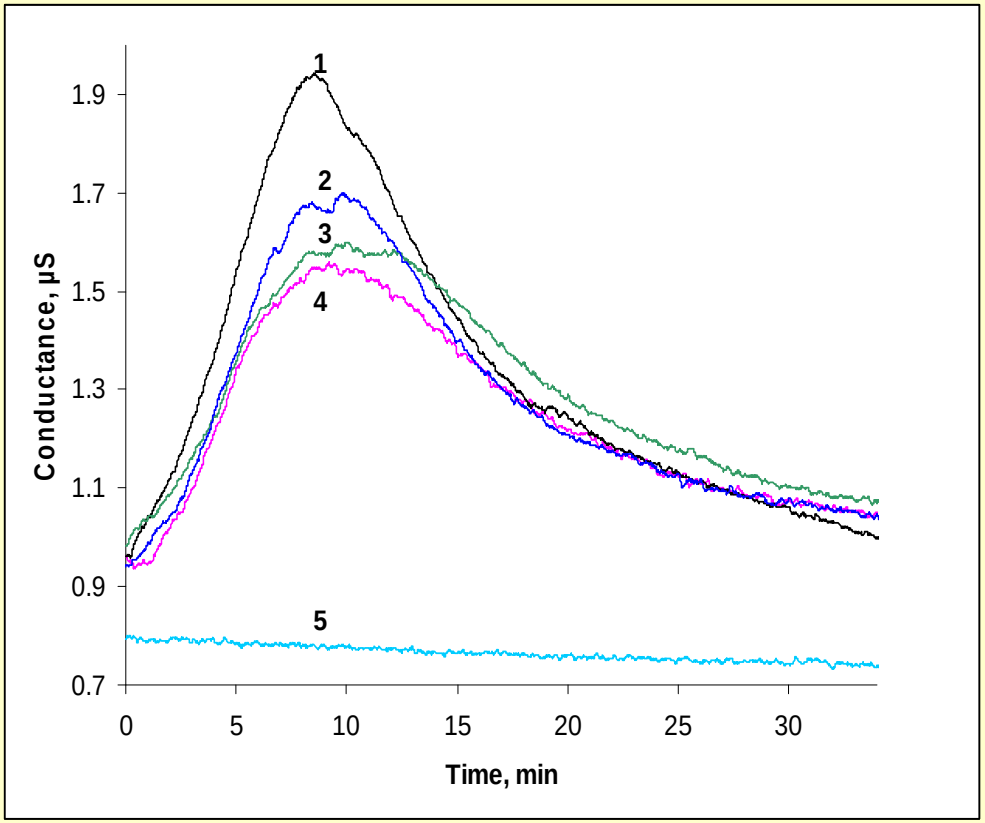
Levoglucosan, a common component of wood smoke, goes similarly

Cellulose



Levoglucosan

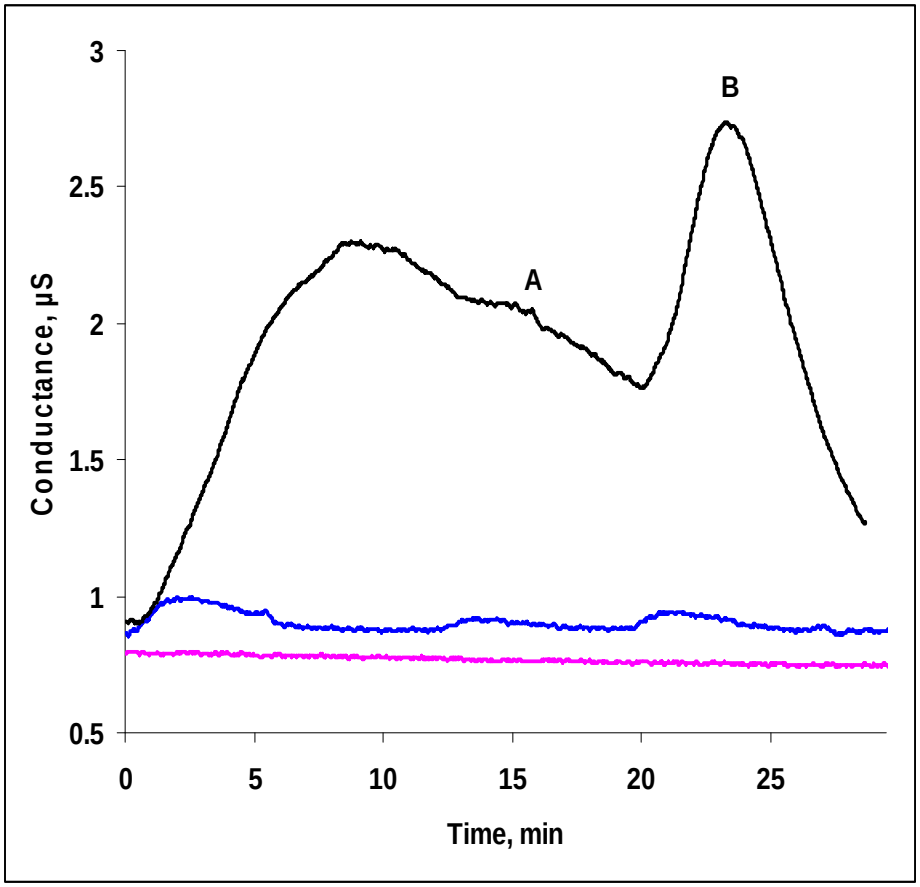
UV Reflectivity of Different Materials



➔ **Teflon tape has the best reflective ability for VU light.**

1. Teflon tape; 2. Teflon tube; 3. Aluminum foil; 4. no covering; 5. no UV. Sample used: 0.8 mM Glu. Keep carrier gas continually pass through the reactor.

Aromatics: Oxidative Ability Test of TiO_2 and $Na_2S_2O_8$ for KHP



➔ • TiO_2 + UV cannot rapidly oxidize KHP under present condition.

➔ • $S_2O_8^{2-}$ has potential to decompose KHP rapidly.

Purple: DI W with no UV, TiO2, and $Na_2S_2O_8$; Blue: DI W with UV, TiO2, and $Na_2S_2O_8$; Black: KHP with UV, TiO2, and $Na_2S_2O_8$. A: TiO_2 Peak; B: $Na_2S_2O_8$ peak.

ACKNOWLEDGMENTS

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U.S. EPA - Science To Achieve Results (STAR) Program

Grant # RD- 83107401-0