Kinetics of Submicron Oleic Acid Aerosols with Ozone; a Novel Aerosol Mass Spectrometric Technique

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Abstract. The reaction kinetics of submicron oleic (9-octadecanoic (Z)-) acid aerosols with ozone was studied using a novel aerosol mass spectrometric technique. In the apparatus a flow of size-selected aerosols is introduced into a flow reactor where the particles are exposed to a known density of ozone for a controlled period of time. The aerosol flow is then directed into an aerosol mass spectrometer for particle size and composition analyses. Data from these studies were used to: (a) quantitatively model the size-dependent kinetics process, (b) determine the aerosol size change due to uptake of ozone, (c) assess reaction stoichiometry, and (d) obtain qualitative information about the volatility of the reaction products. The reactive uptake probability for ozone on oleic acid particles obtained from modeling is 1.6 (–0.2) x 10^{-3} with an upper limit for the reacto-diffusive length of ~10 nm. Atmospheric implications of the results are discussed.

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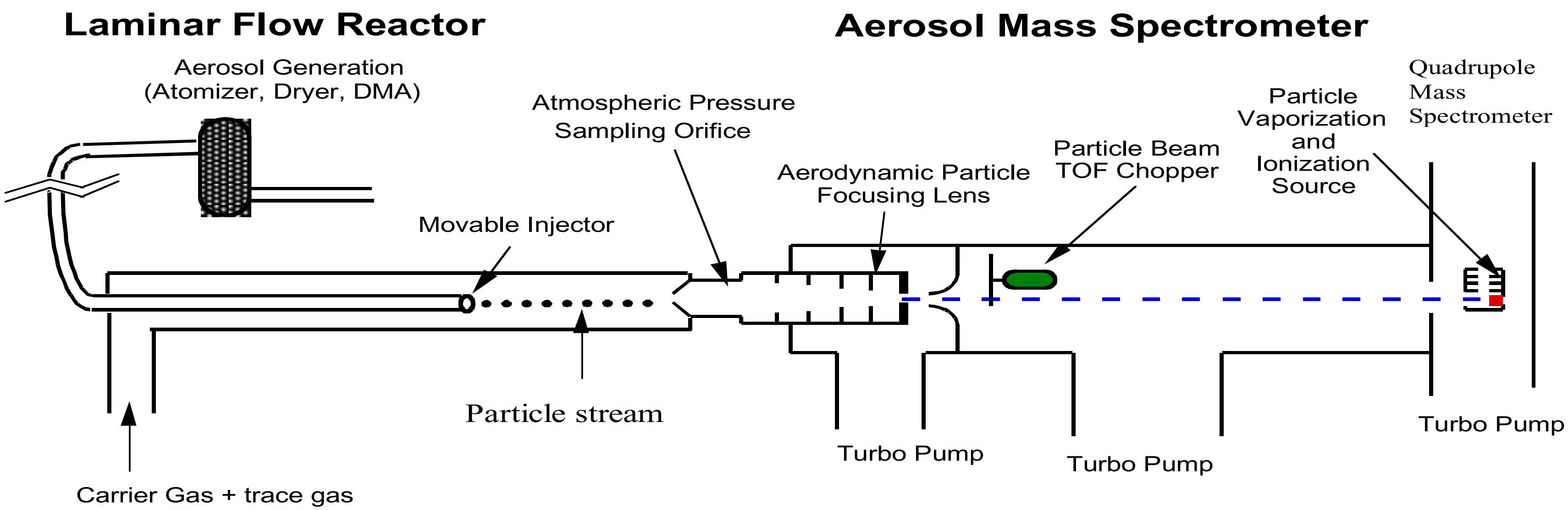
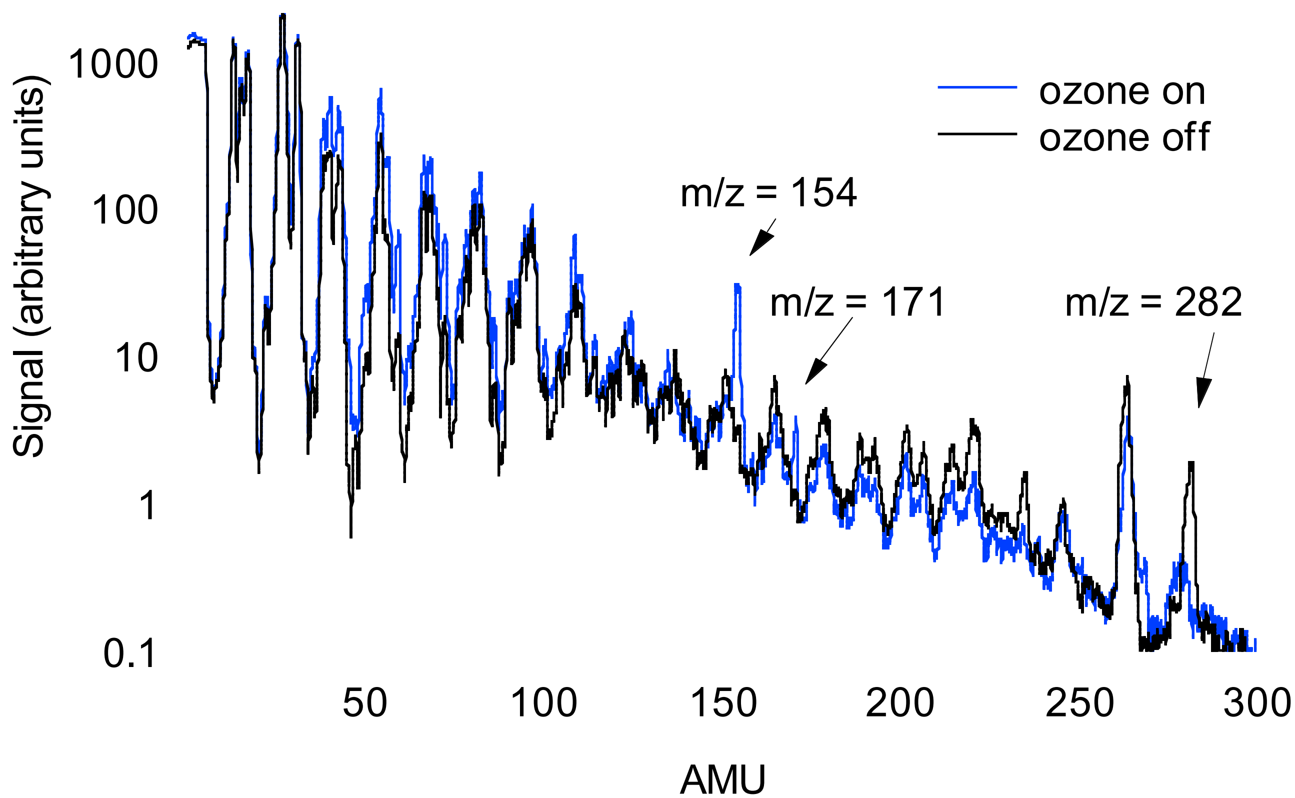
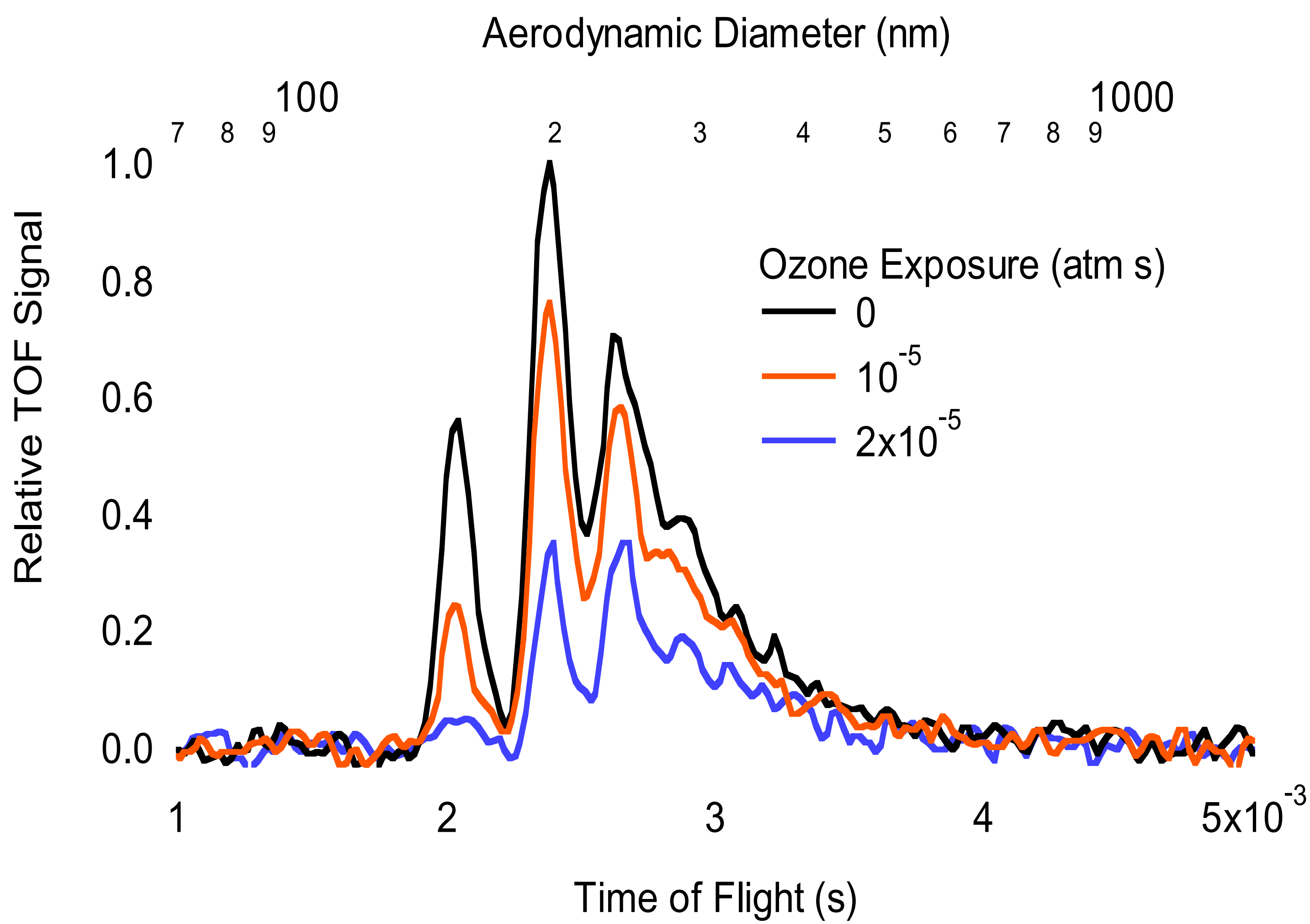


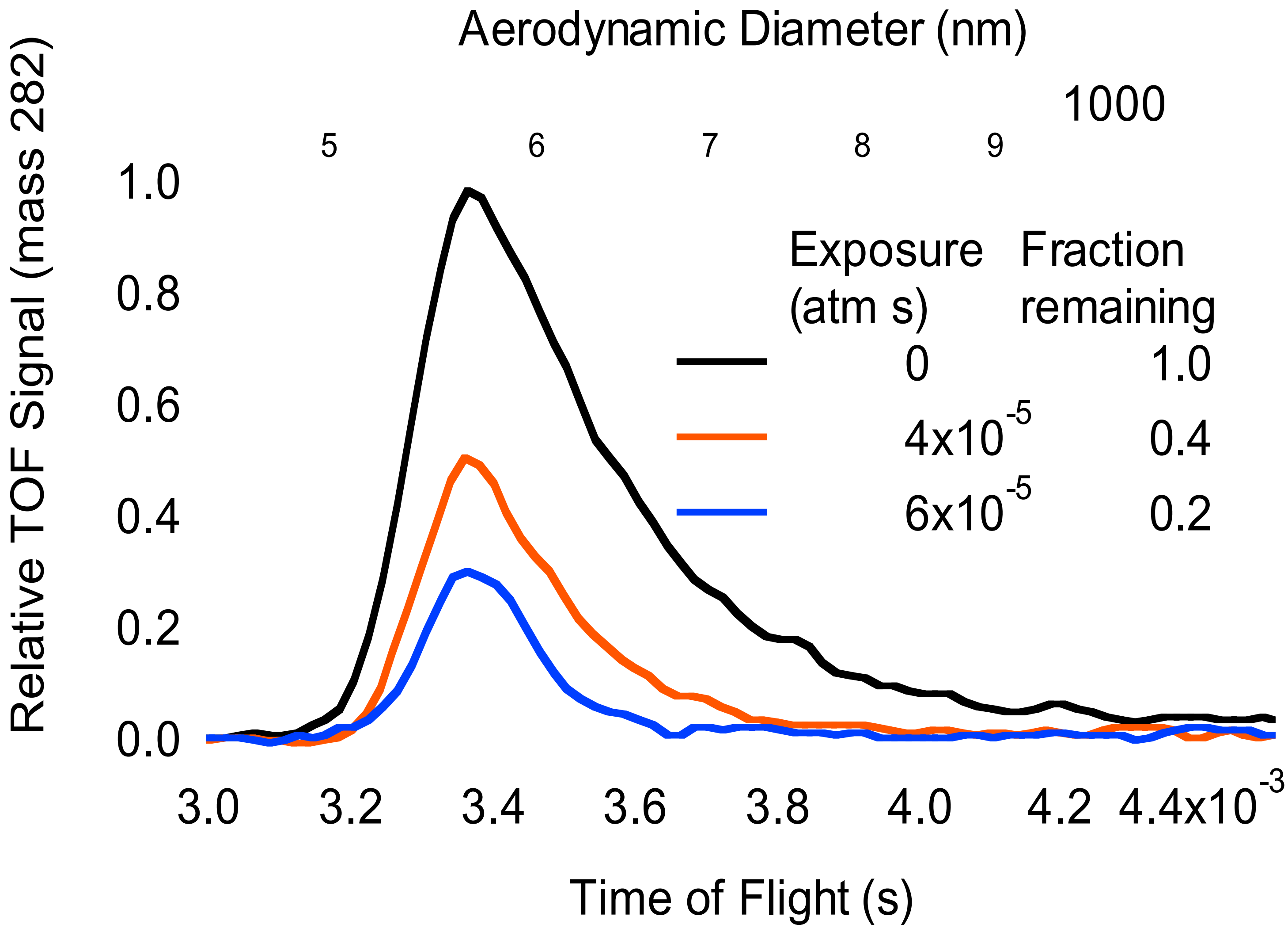
Laminar Flow Reactor
Aerosol Mass Spectrometer
Aerosol Generation
(Atomizer, Dryer, DMA)
Atmospheric Pressure
Sampling Orifice
Quadrupole
Mass
Spectrometer
Particle
Vaporization
and
Ionization
Source
Particle Beam
TOF Chopper
Aerodynamic Particle
Focusing Lens
Movable Injector
Particle stream
Carrier Gas + trace gas
Turbo Pump
Turbo Pump
Turbo Pump



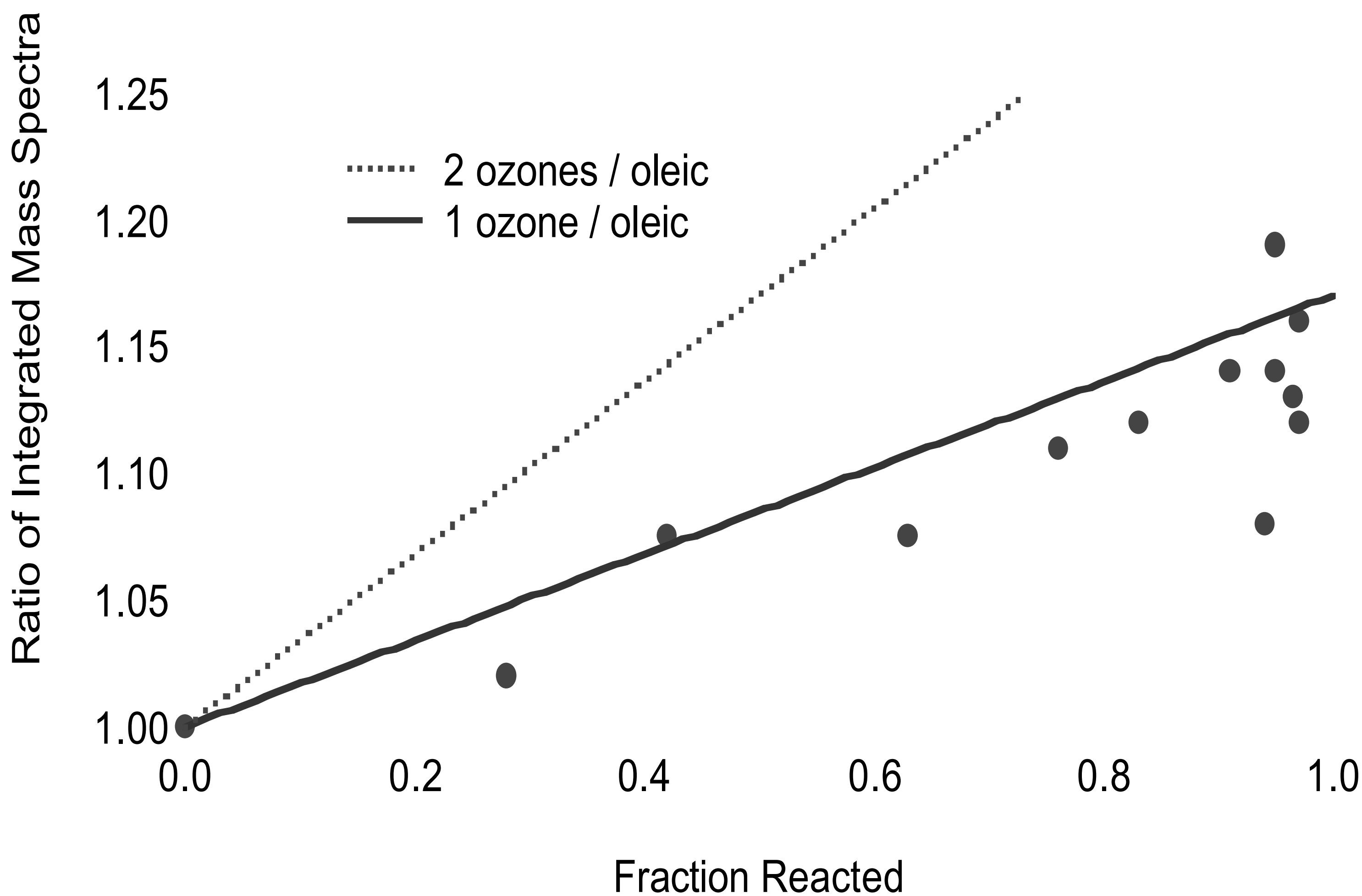
1000
100
10
1
0.1
Signal (arbitrary units)
50
100
150
200
250
300
AMU
ozone on
ozone off
m/z = 154
m/z = 171
m/z = 282



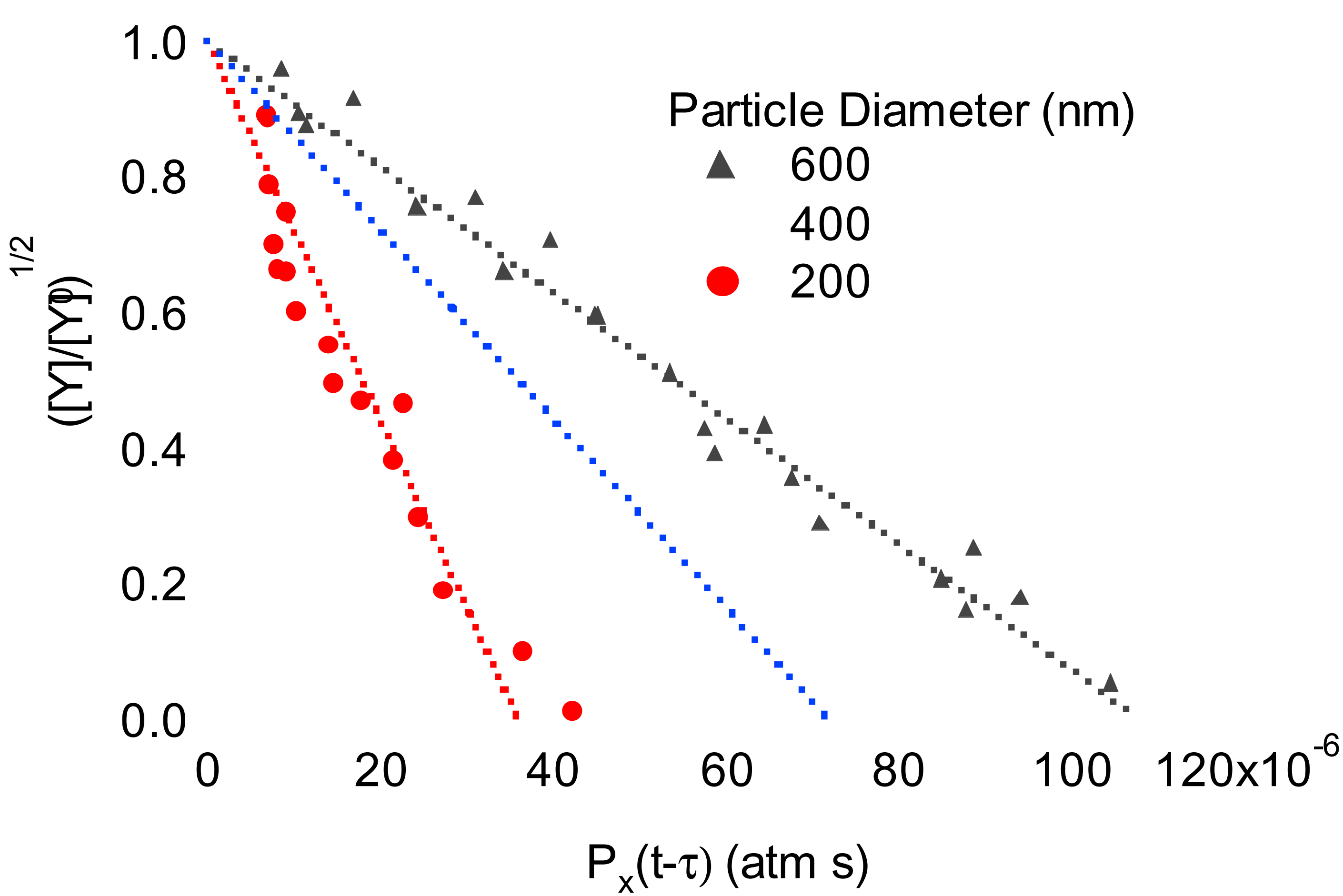
Aerodynamic Diameter (nm)
100
1000
7
8
9
2
3
4
5
6
7
8
9
1.0
0.8
0.6
0.4
0.2
0.0
Relative TOF Signal
Ozone Exposure (atm s)
0
10-5
2x10-5
1
2
3
4
5x10-3
Time of Flight (s)



Aerodynamic Diameter (nm)
1000
5
6
7
8
9
1.0
0.8
0.6
0.4
0.2
0.0
Relative TOF Signal (mass 282)
Exposure (atm s)
Fraction remaining
0
1.0
4x10^-5
0.4
6x10^-5
0.2
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4x10^-3
Time of Flight (s)



Ratio of Integrated Mass Spectra
1.25
1.20
1.15
1.10
1.05
1.00
2 ozones / oleic
1 ozone / oleic
0.0
0.2
0.4
0.6
0.8
1.0
Fraction Reacted



Particle Diameter (nm)
600
400
200
1.0
0.8
0.6
0.4
0.2
0.0
([Y]/[Y]0)^1/2
0
20
40
60
80
100
120x10^-6
Px(t-τ) (atm s)

Laboratory Studies of Sulfuric Acid Aerosol Formation, Growth, and Coagulation

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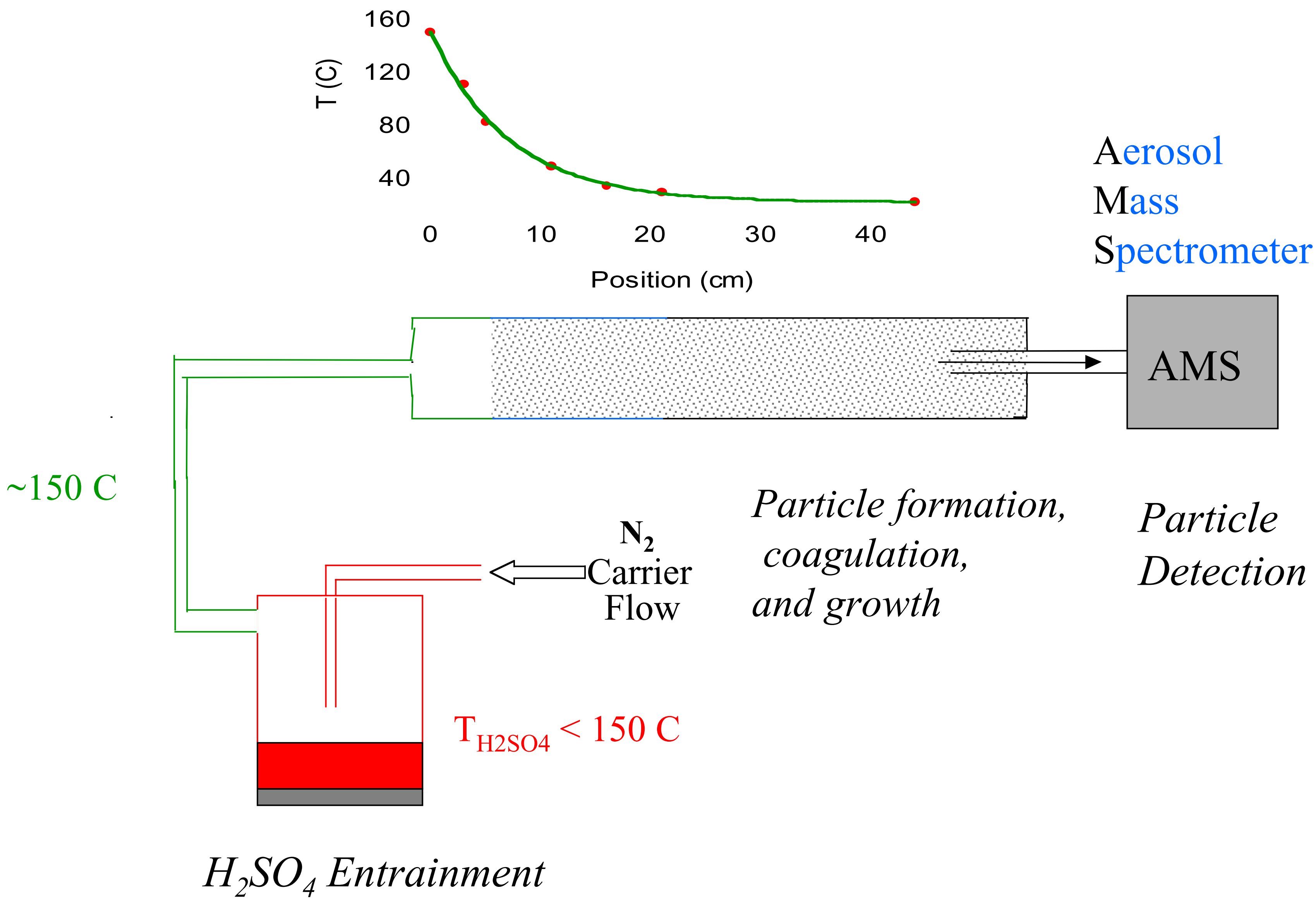
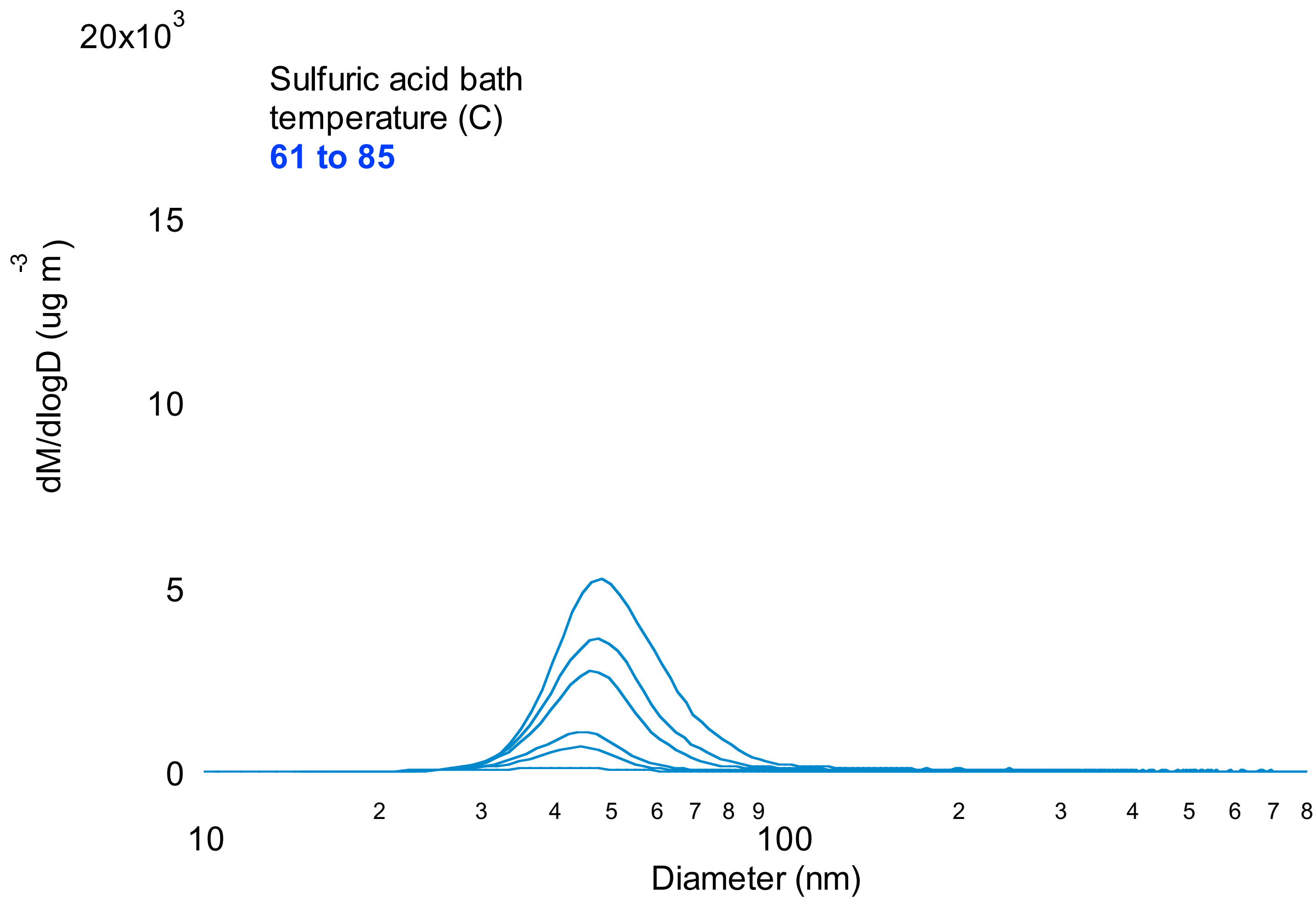
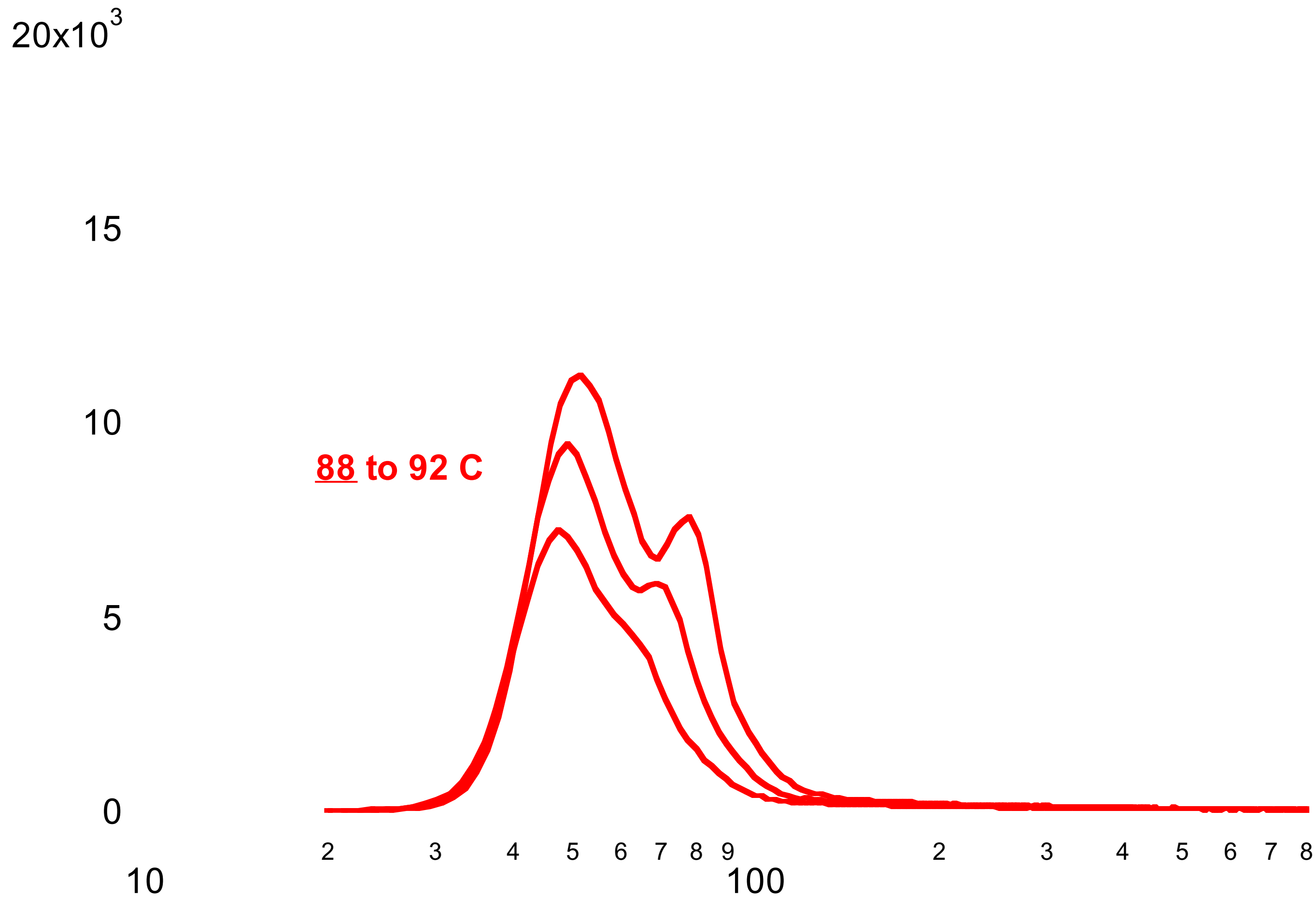
Abstract. Laboratory measurements involving nucleation, condensation, and coagulation of sulfuric acid are described. Studies were carried out using a laminar flowtube at atmospheric pressure coupled to an aerosol mass spectrometer (AMS). A sulfuric acid reservoir heated to a known temperature was connected to the flowtube via heated tubing. Dry filtered nitrogen carrier gas was pre-heated and passed over the reservoir entraining an equilibrium density of the H_2SO_4(g) to the flowtube. The entrance to the flowtube was heated to a temperature above that of the reservoir, establishing a well-characterized decreasing temperature profile along the flowtube axis. Supersaturation (and consequent nucleation and growth) conditions were reached at a position within the flowtube determined by the temperature profile and the H_2SO_4 vapor pressure. The number and mass distributions of the particles formed in this way were measured on-line by the AMS at the flowtube exit. With the entrance of the flowtube at 150 C, particles were first observed at a H_2SO_4 vapor pressure of 10^{-4} torr forming particles at a number density of 10^4 cm^{-3}. As the pressure increased to $3x10^{-2}$ torr, the particle number density increased to 10^7 cm^{-3}. However, the median diameter increased only from 40 to 50 nm. At pressures higher than $4x10^{-3}$ torr, the size distributions were observed to exhibit broadening and a new mode appeared near 60nm, consistent with coagulation. A third mode appeared at H_2SO_4 pressures near $3x10^{-2}$ torr indicating further coagulation. This work is a first time *on-line* laboratory observation of sulfuric acid microphysics spanning nucleation and coagulation processes. The features of the apparatus enabling absolute detection of mass and number distributions will be discussed.

Experimental Apparatus

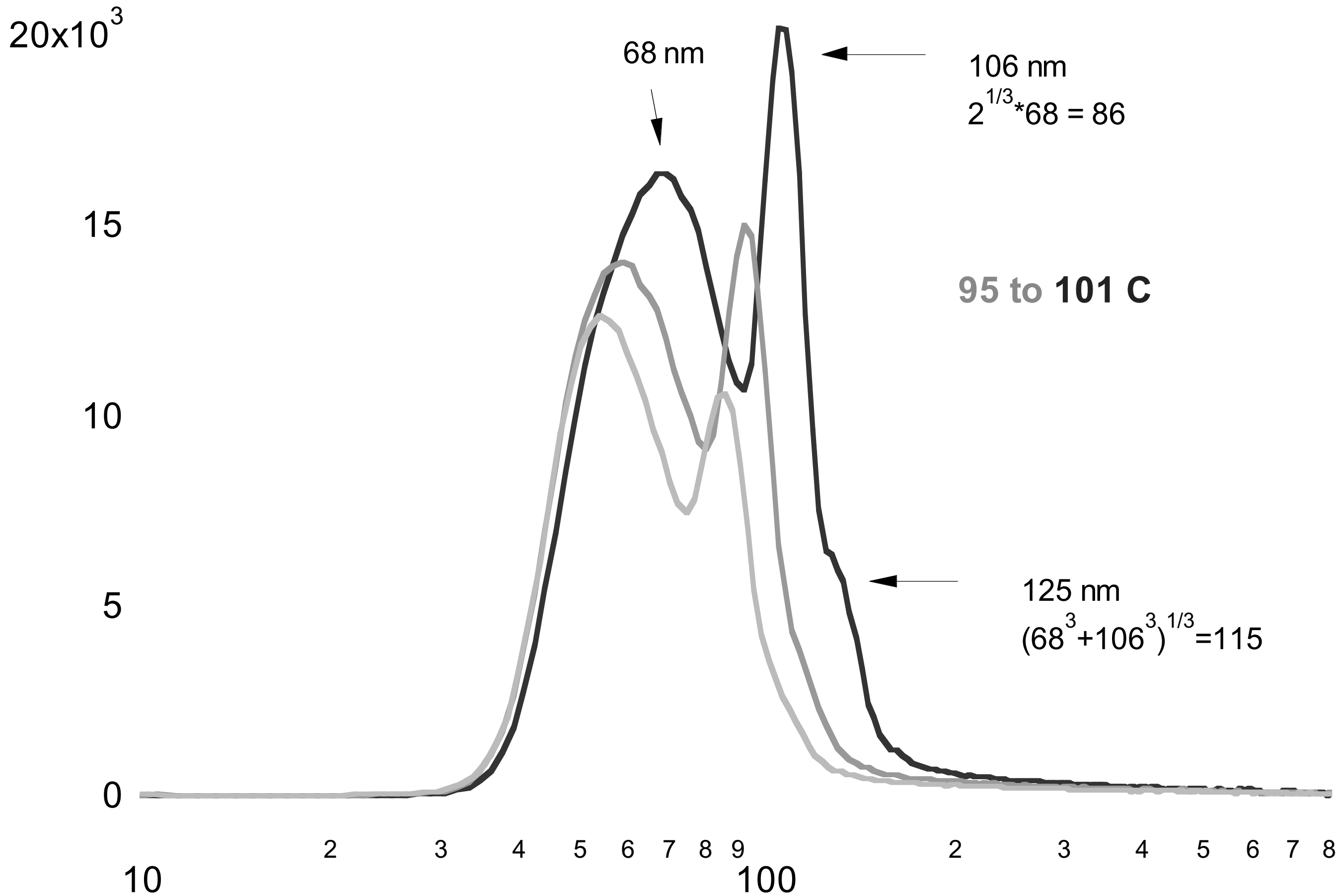




20x10^3
15
10
5
0
Sulfuric acid bath
temperature (C)
61 to 85
dM/dlogD (ug m^-3)
2
3
4
5
6
7
8
9
10
100
Diameter (nm)



20x10^3
15
10
5
0
88 to 92 C
2
3
4
5
6
7
8
9
2
3
4
5
6
7
8
10
100


20x10^3
15
10
5
0
68 nm
106 nm
2^1/3*68 = 86
95 to 101 C
125 nm
(68^3+106^3)^1/3=115
2
3
4
5
6
7
8
9
2
3
4
5
6
7
8
10
100