Laboratory Studies of Aerosol Optical Properties

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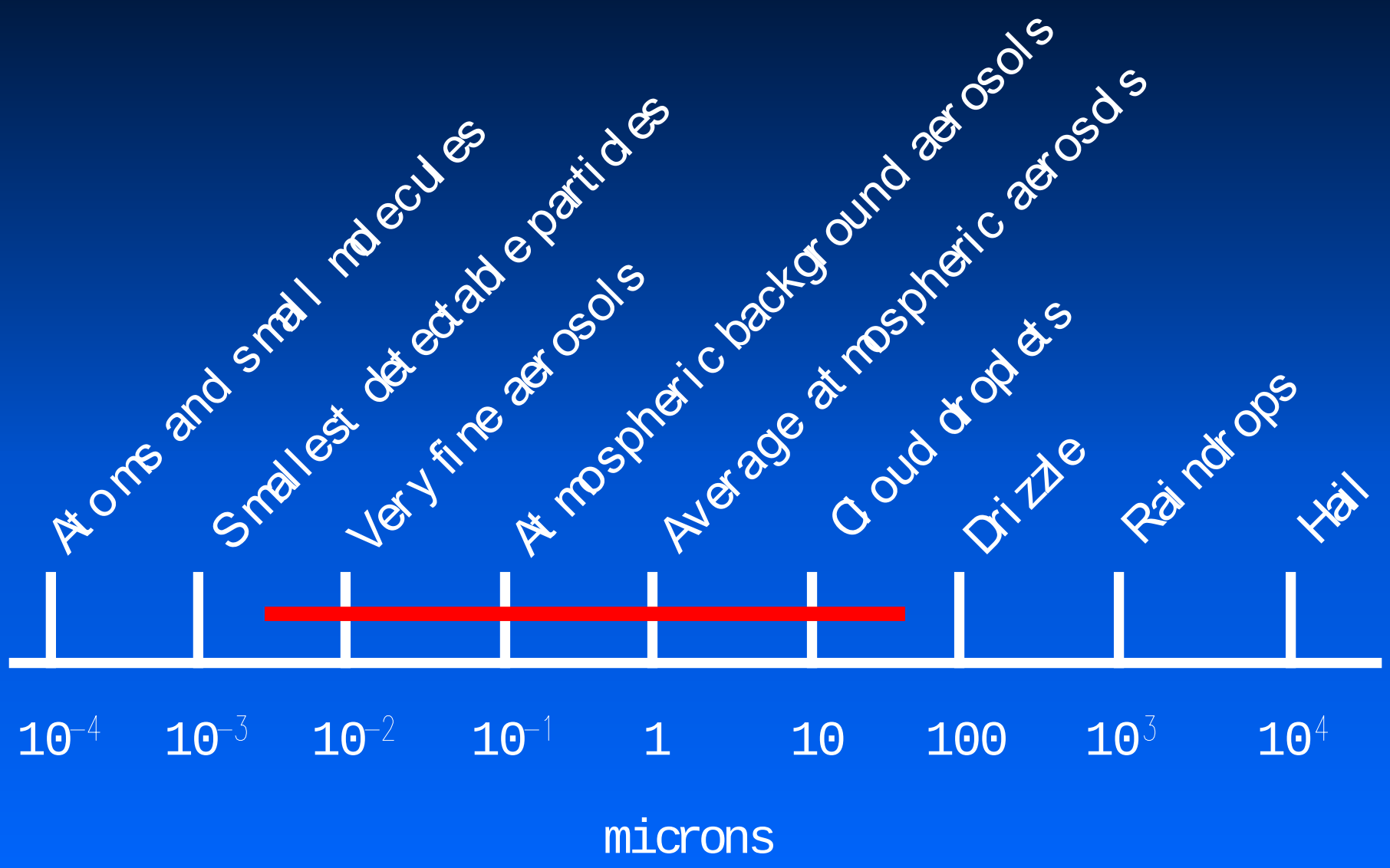
Particle Size



Laboratory Studies

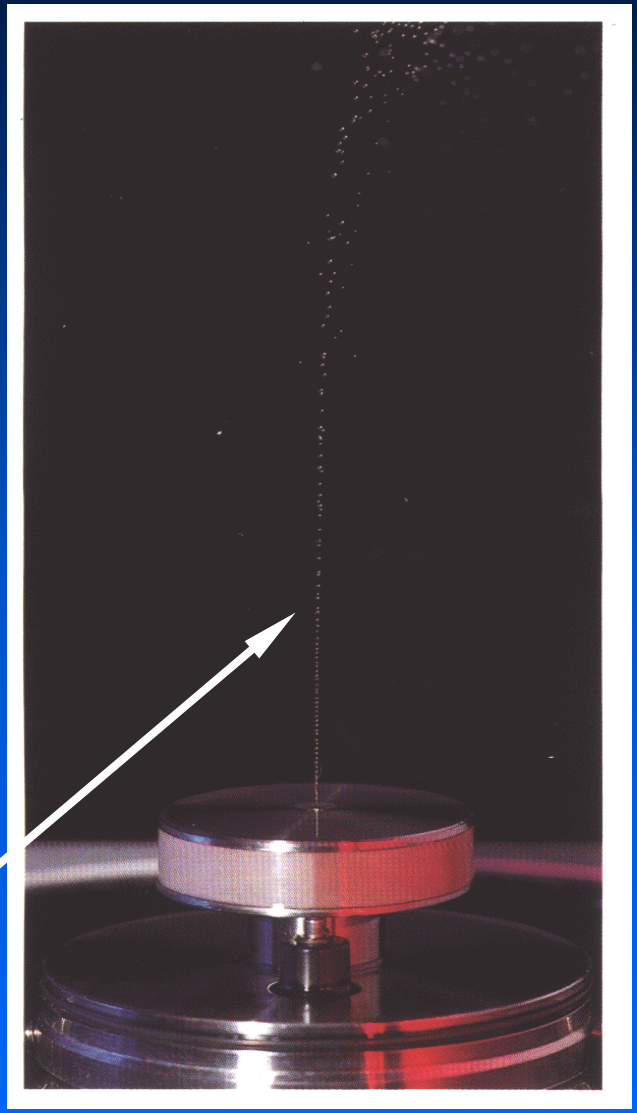
- Produce aerosols in the laboratory
  - Relevant inorganic and organic species
- Subject aerosols to appropriate conditions
  - e.g., temperature, pressure, and humidity
- Use spectroscopy to study aerosol properties
  - Chemical
  - Physical
  - Optical

Aerosol Production

- Aerosol source characteristics
  - Composition control
  - Size control
  - Throughput control
  - Stability
- Many types of aerosol sources exist to suit the needs of almost any laboratory experiment

Aerosol Production

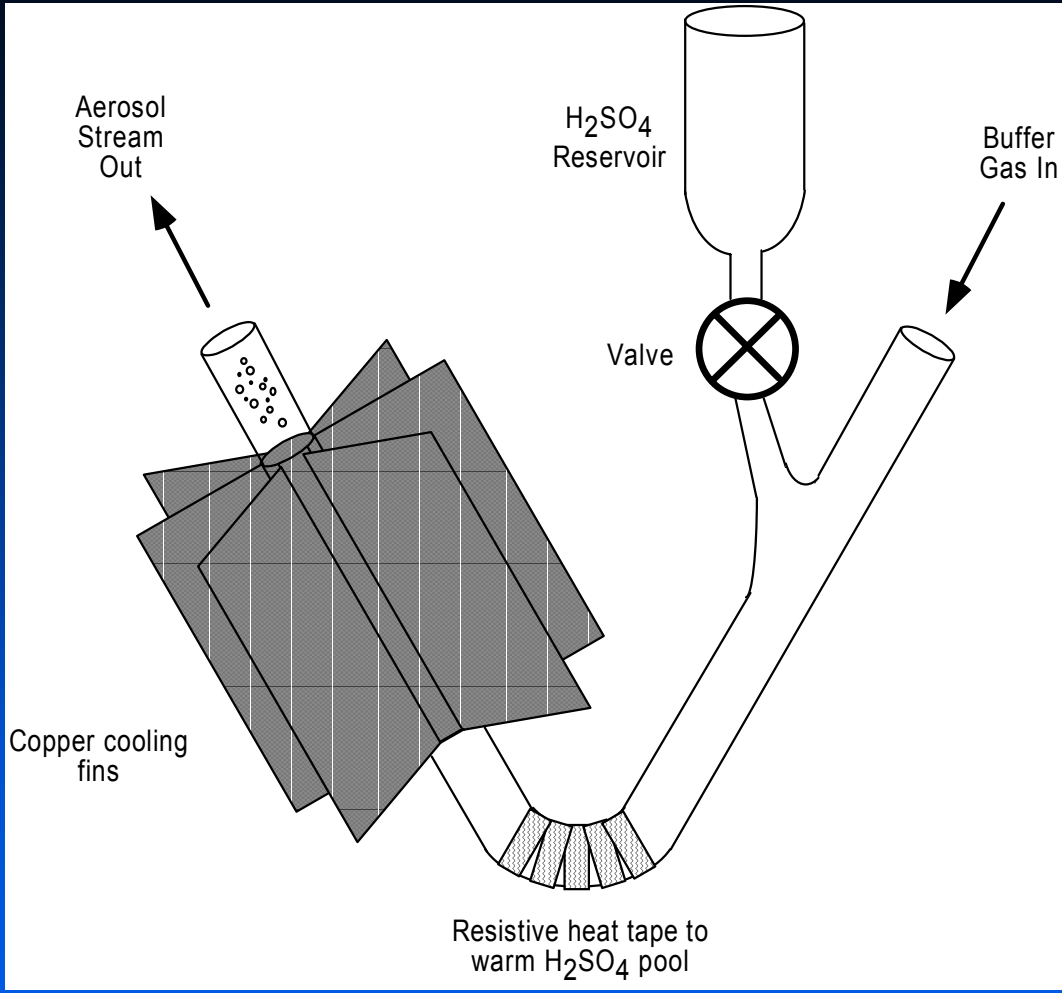
- Mechanical sources
  - Vibrating orifice aerosol generators (VOAG's)
  - Nebulizers
  - Bubblers
  - Brush generators



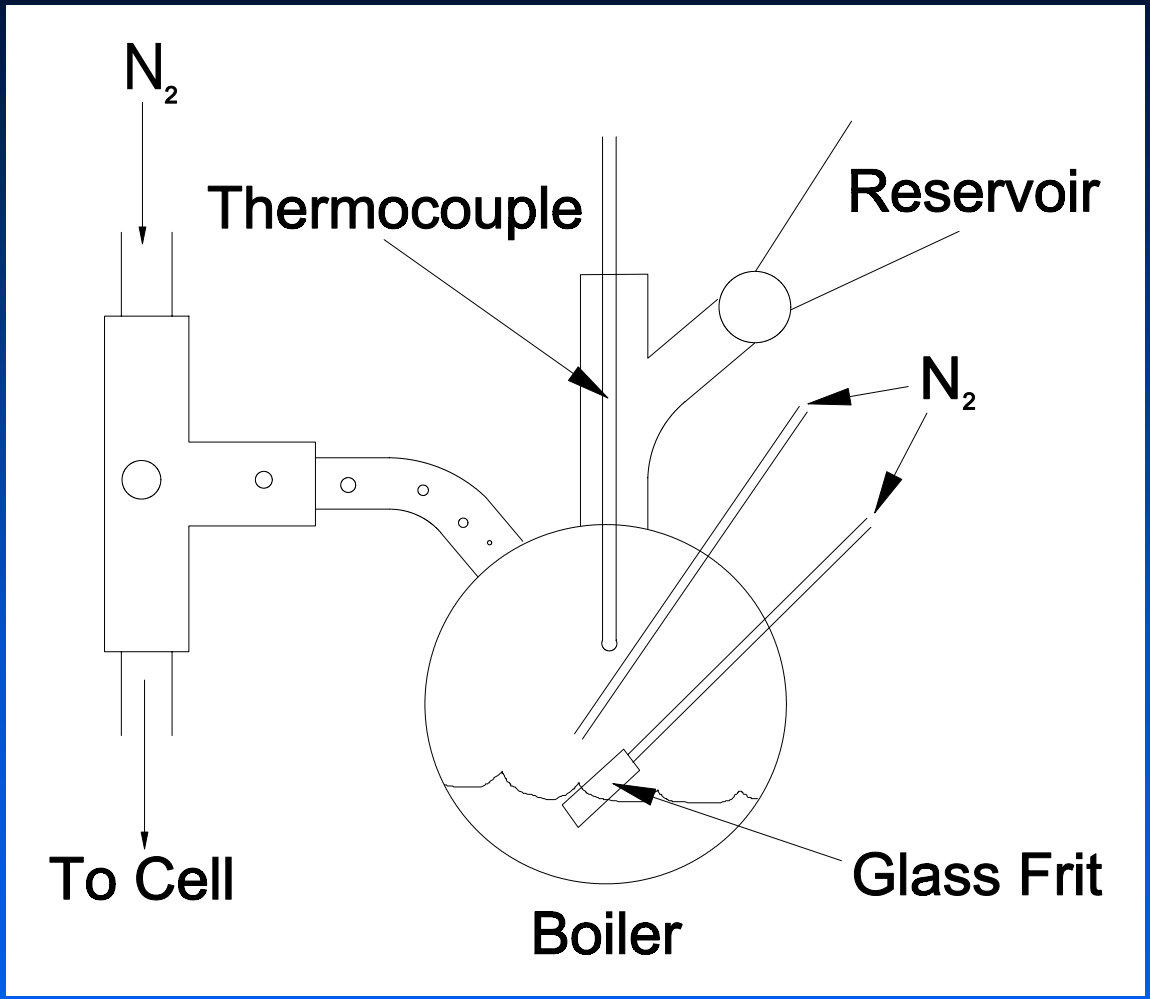
VOAG in action. (Courtesy of TSI, Inc.)

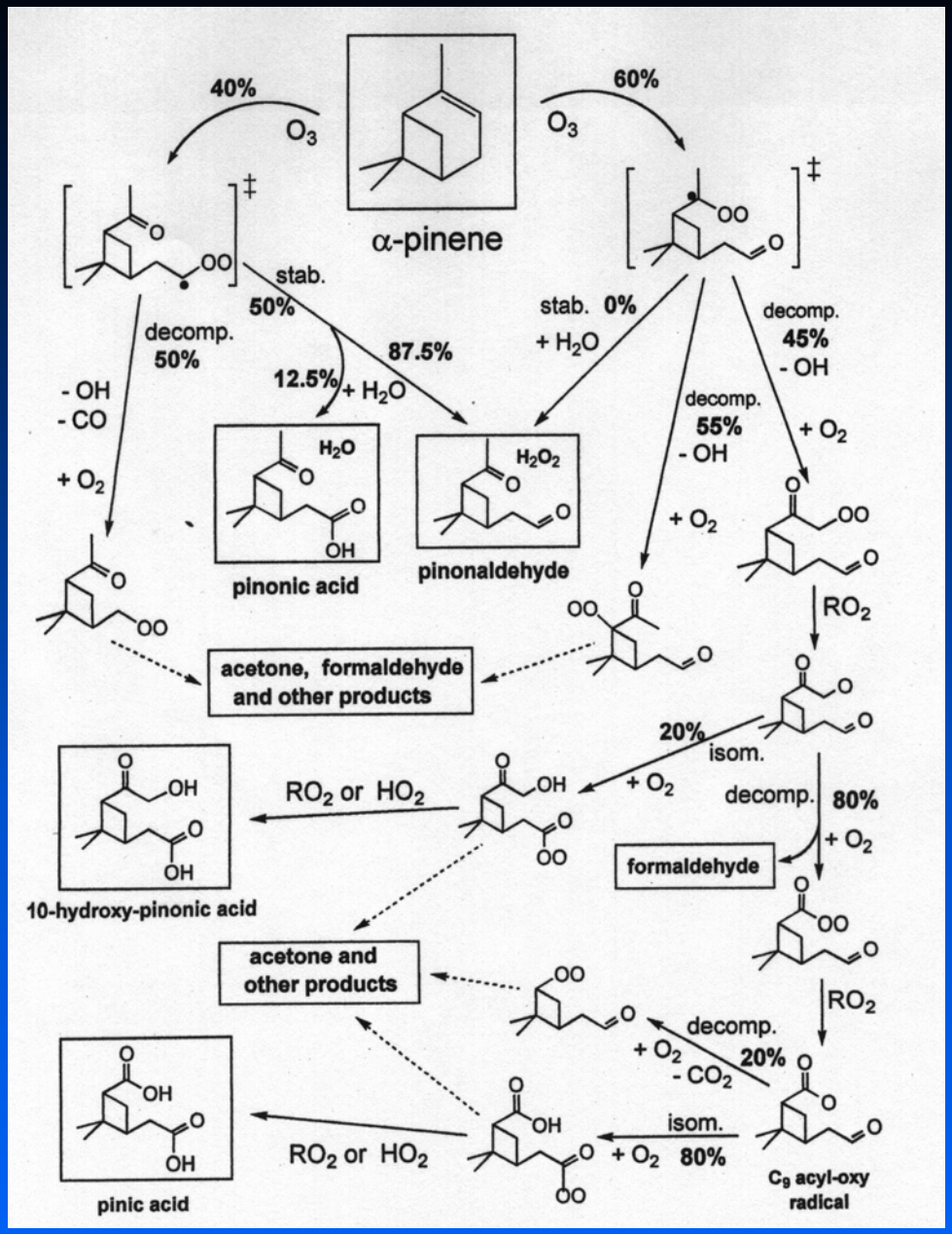
Aerosol Production

- Nucleation sources
  - Heterogeneous
    - Condensation of vapor on preexisting particles
  - Homogeneous
    - Primary source
      - Cooling of supersaturated vapors
    - Secondary
      - Chemical reactions



Adapted from Lovejoy, *et al.*, *J. Geophys. Res.*, **100**, 18775–18,780, (1995).


N_2
Thermocouple
Reservoir
N_2
To Cell
Glass Frit
Boiler



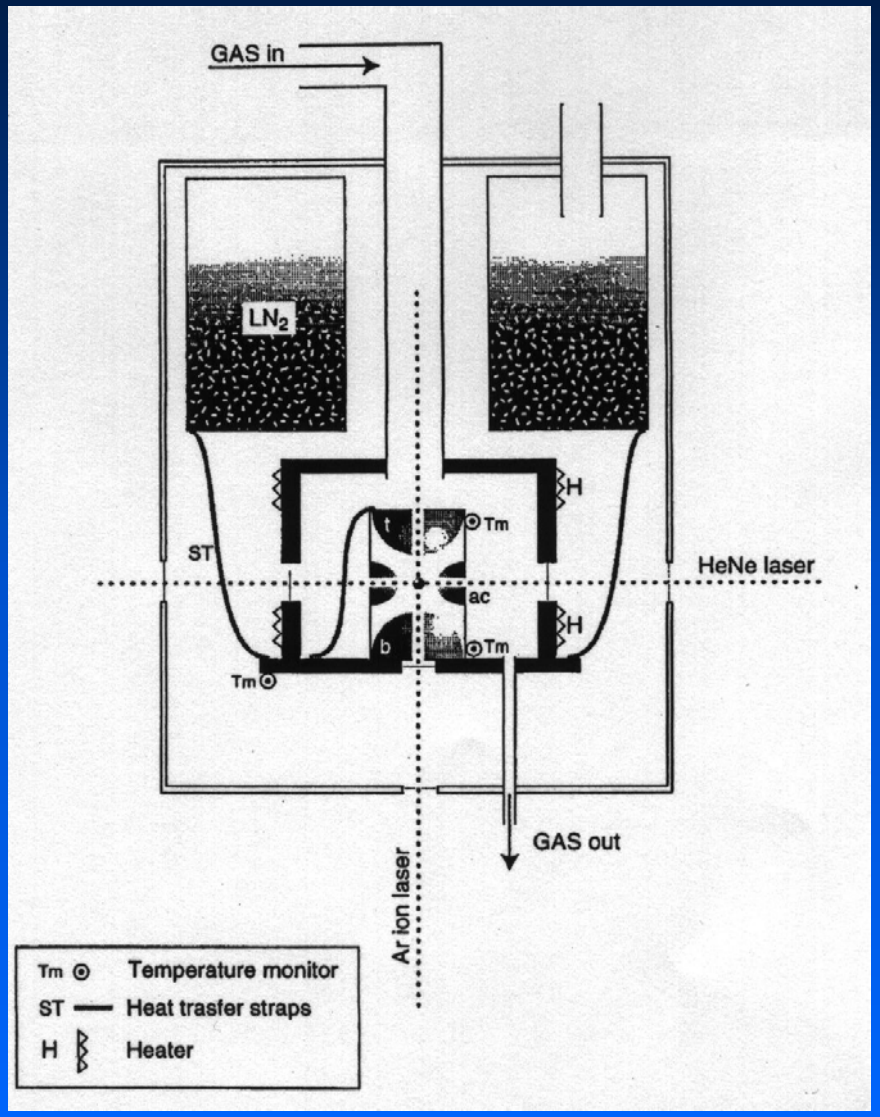
Jenkin, *et al.*, *Atmos. Env.*, **34**, 2837–2850, (2000)

Aerosol Conditioning

- Conditioning after aerosol production
  - (De)humidification
  - Temperature processing
  - Chemical processing
    - Internally mixed aerosols
    - Coated or stratified aerosols

Aerosol Instruments

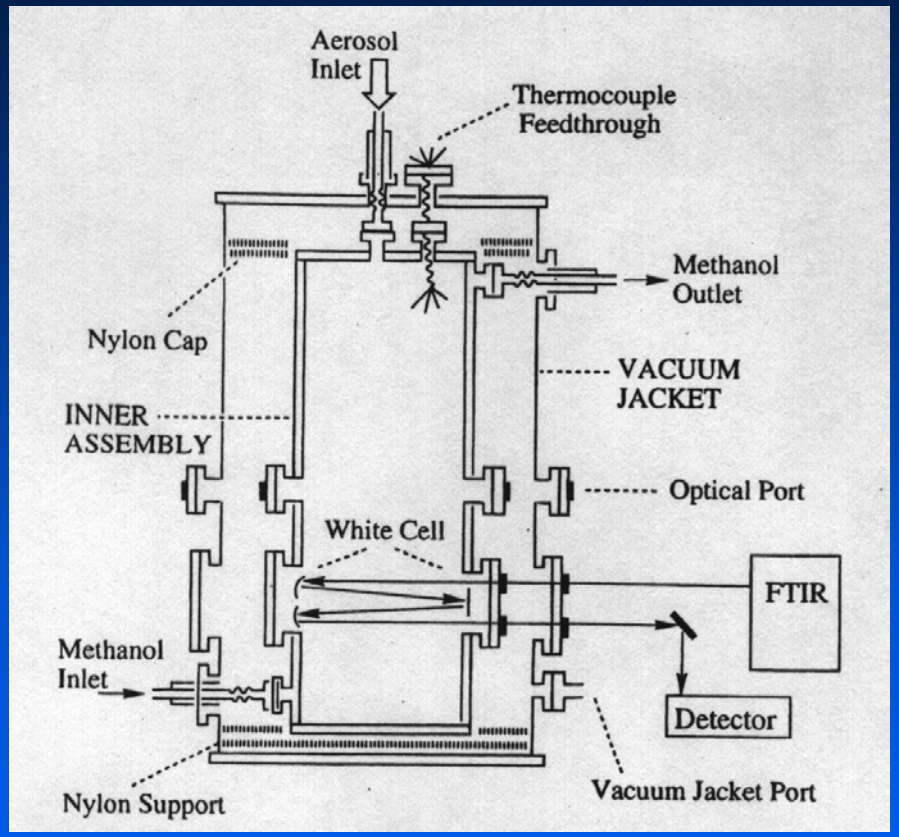
- Single particle traps
  - Particle analysis through Mie scattering



Xu, *et al.*, *J. Phys. Chem. B*, **102**, 7462–7469, (1998).

Aerosol Instruments

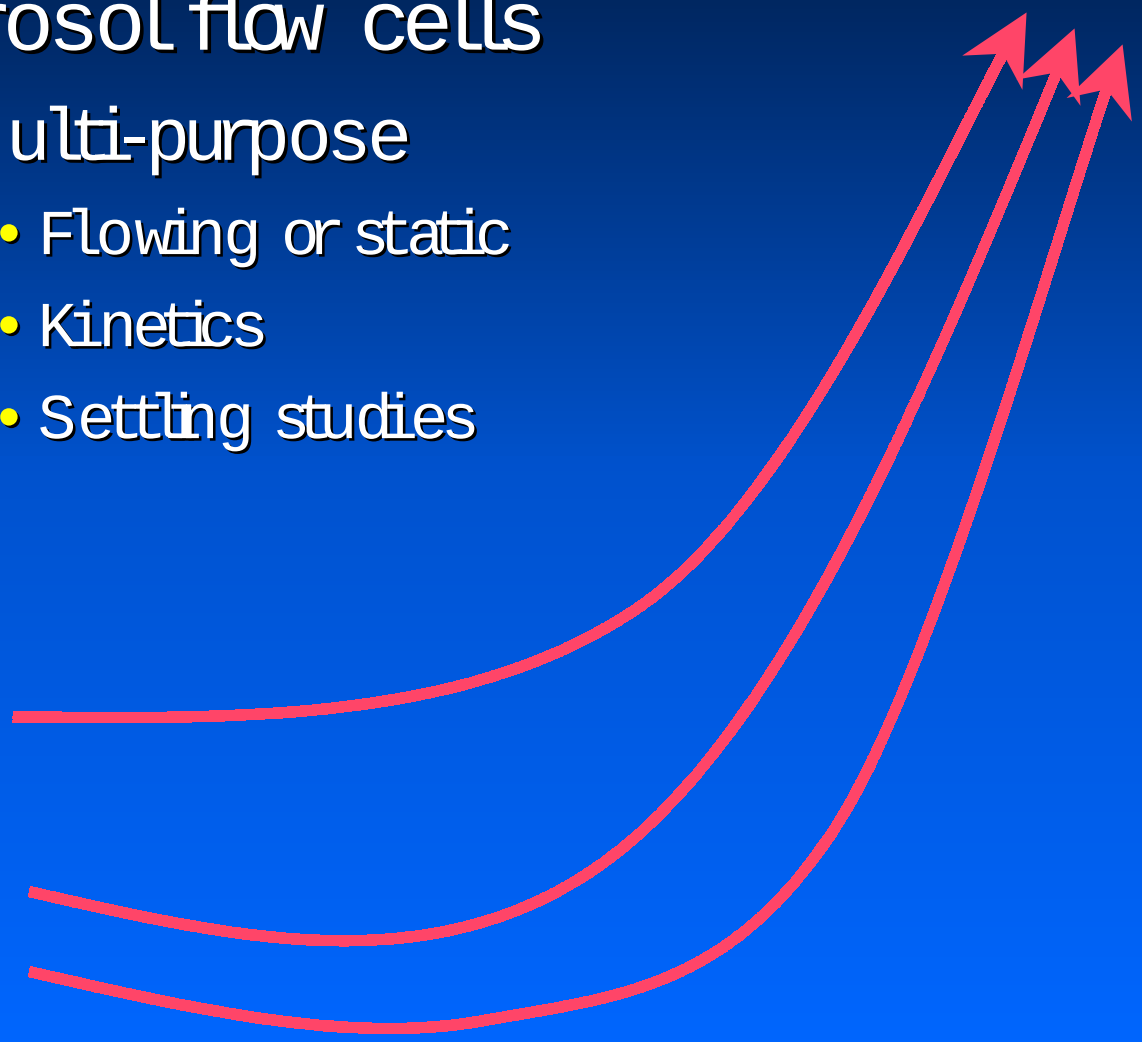
- Aerosol chambers
  - Settling experiments
  - Crystallization experiments

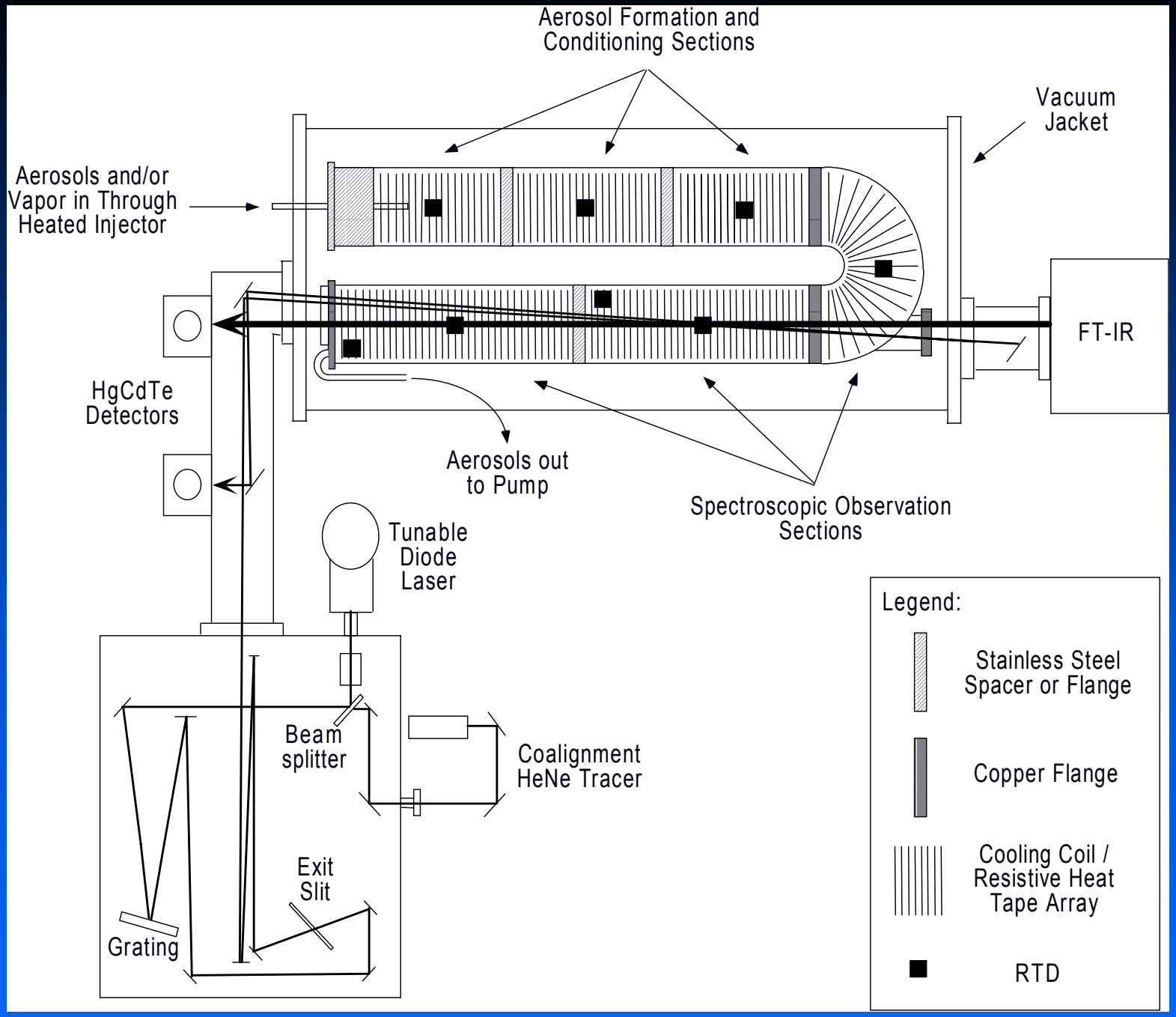


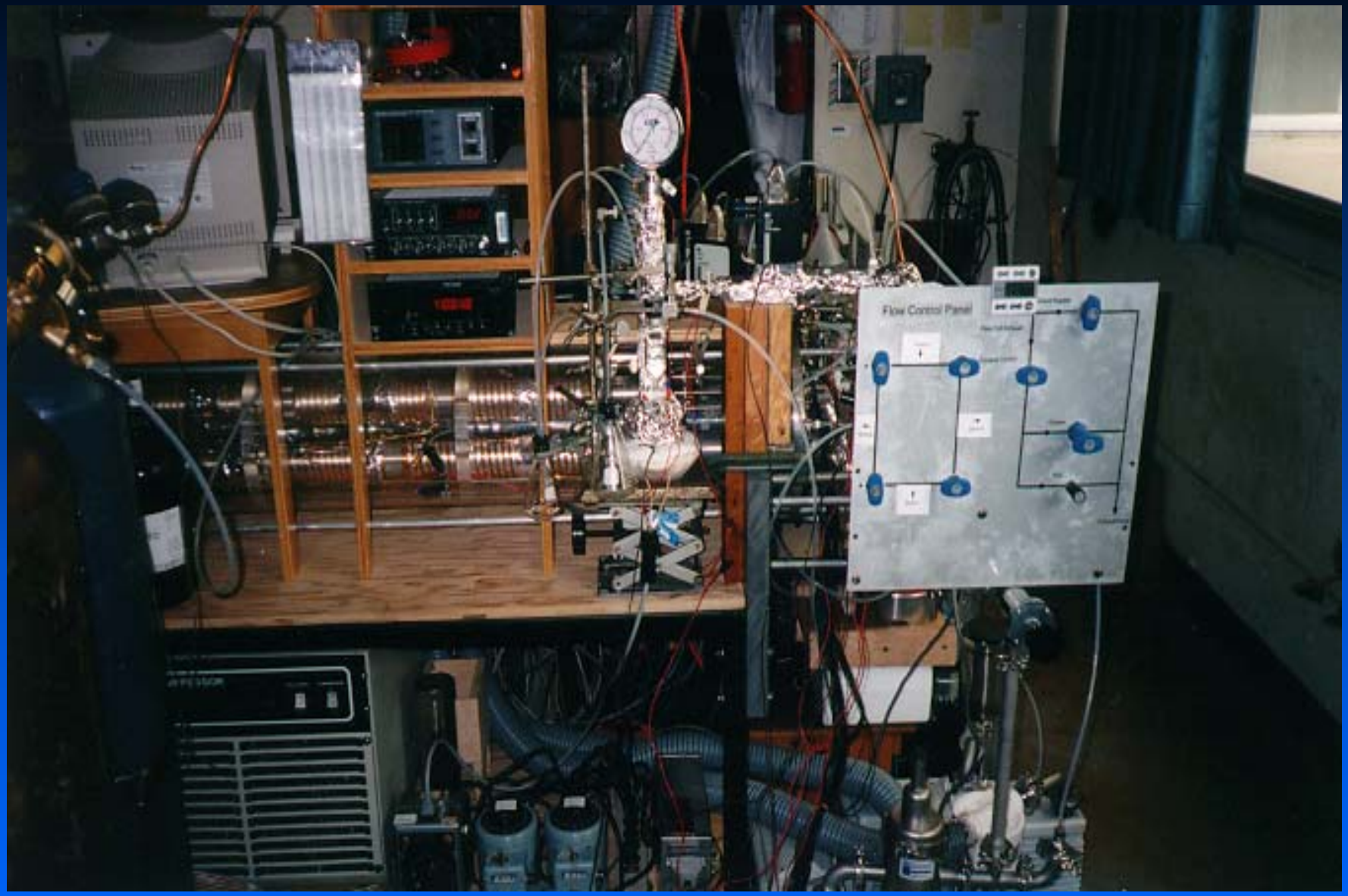
Disselkamp, *et al.*, *J. Phys. Chem.*, **100**, 9127–9137, (1996).

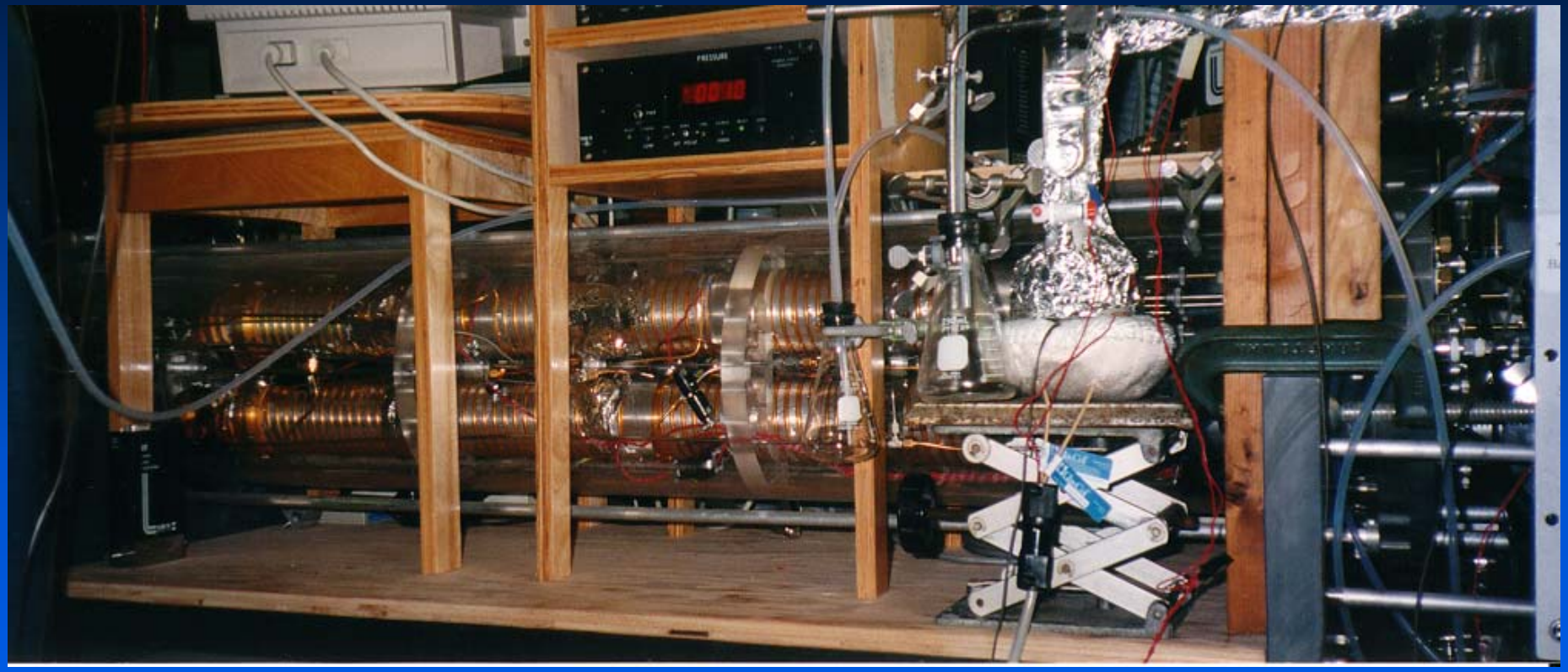
Aerosol Instruments

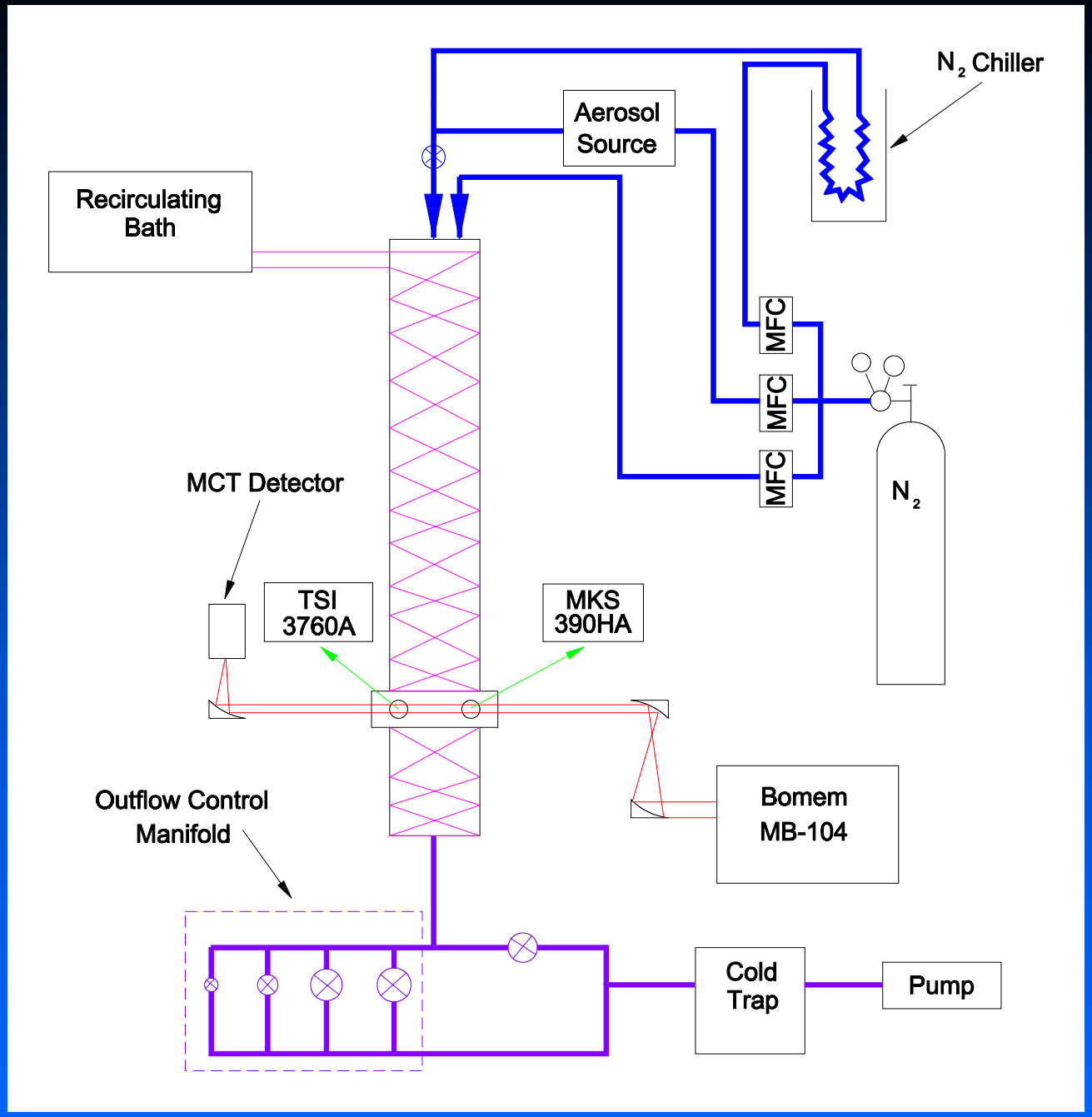
- Aerosol flow cells
  - Multi-purpose
    - Flowing or static
    - Kinetics
    - Settling studies




Aerosol Formation and
Conditioning Sections
Vacuum
Jacket
Aerosols and/or
Vapor in Through
Heated Injector
FT-IR
HgCdTe
Detectors
Aerosols out
to Pump
Spectroscopic Observation
Sections
Tunable
Diode
Laser
Beam
splitter
Coalignment
HeNe Tracer
Exit
Slit
Grating
Legend:
Stainless Steel
Spacer or Flange
Copper Flange
Cooling Coil /
Resistive Heat
Tape Array
RTD


Flow Control Panel


PRESSURE

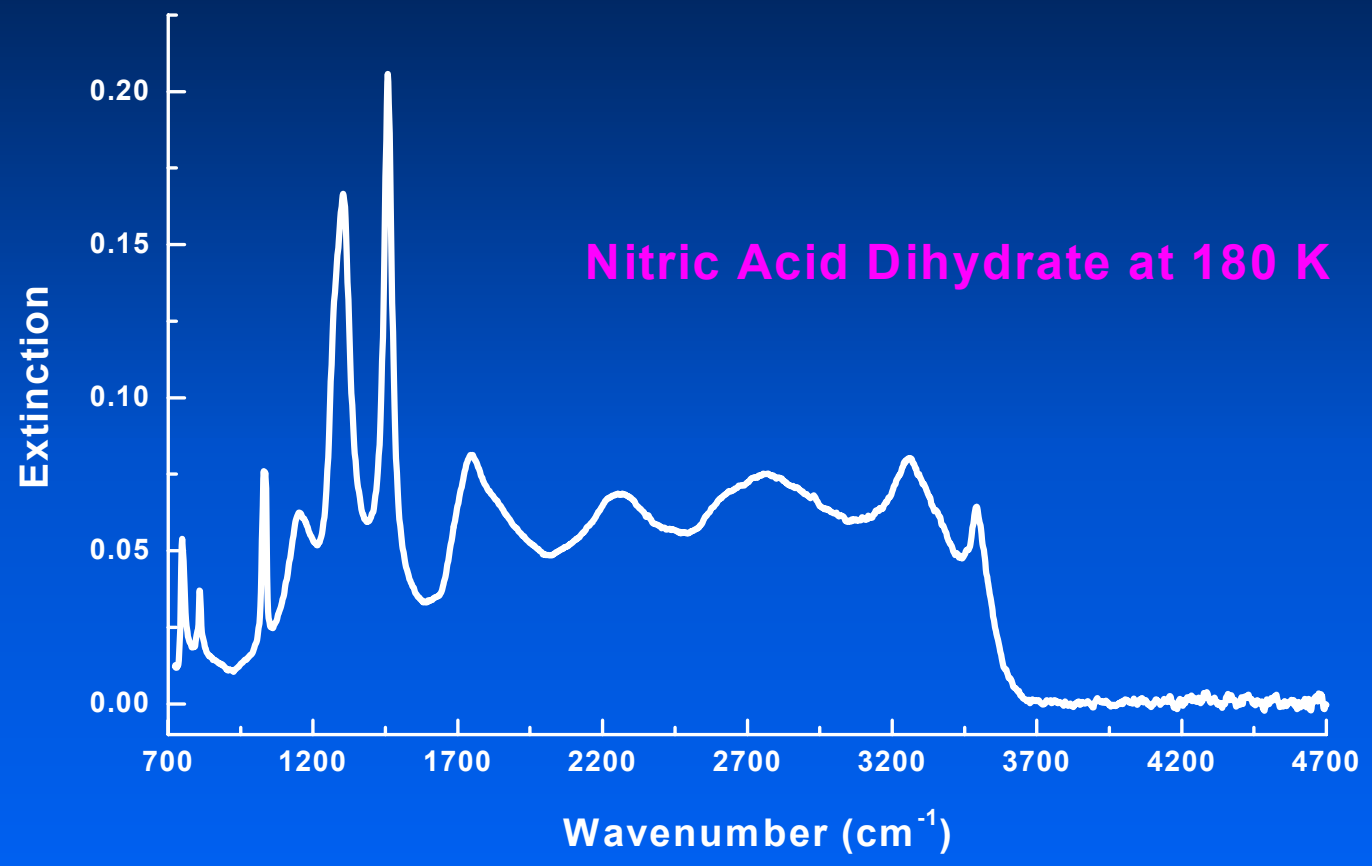

N2 Chiller
Aerosol Source
Recirculating Bath
MFC
MFC
MFC
N2
MCT Detector
TSI 3760A
MKS 390HA
Bomem MB-104
Outflow Control Manifold
Cold Trap
Pump

Fisherbrand
GLASS
Outflow cooled manifold

Aerosol Spectroscopy

- Common link…
- … interaction of electromagnetic radiation with matter!
- Spectroscopy
  - IR
  - UV-Vis
  - Microwave

Aerosol Spectroscopy



Aerosol Spectroscopy

- The previous spectrum is what you might expect from a classic thin-film experiment
  - Extinction ≈ Absorption
- What happens in the case where the particle size is comparable to the wavelength of light passing through it?
  - Extinction = Absorption + Scattering

Aerosol Spectroscopy

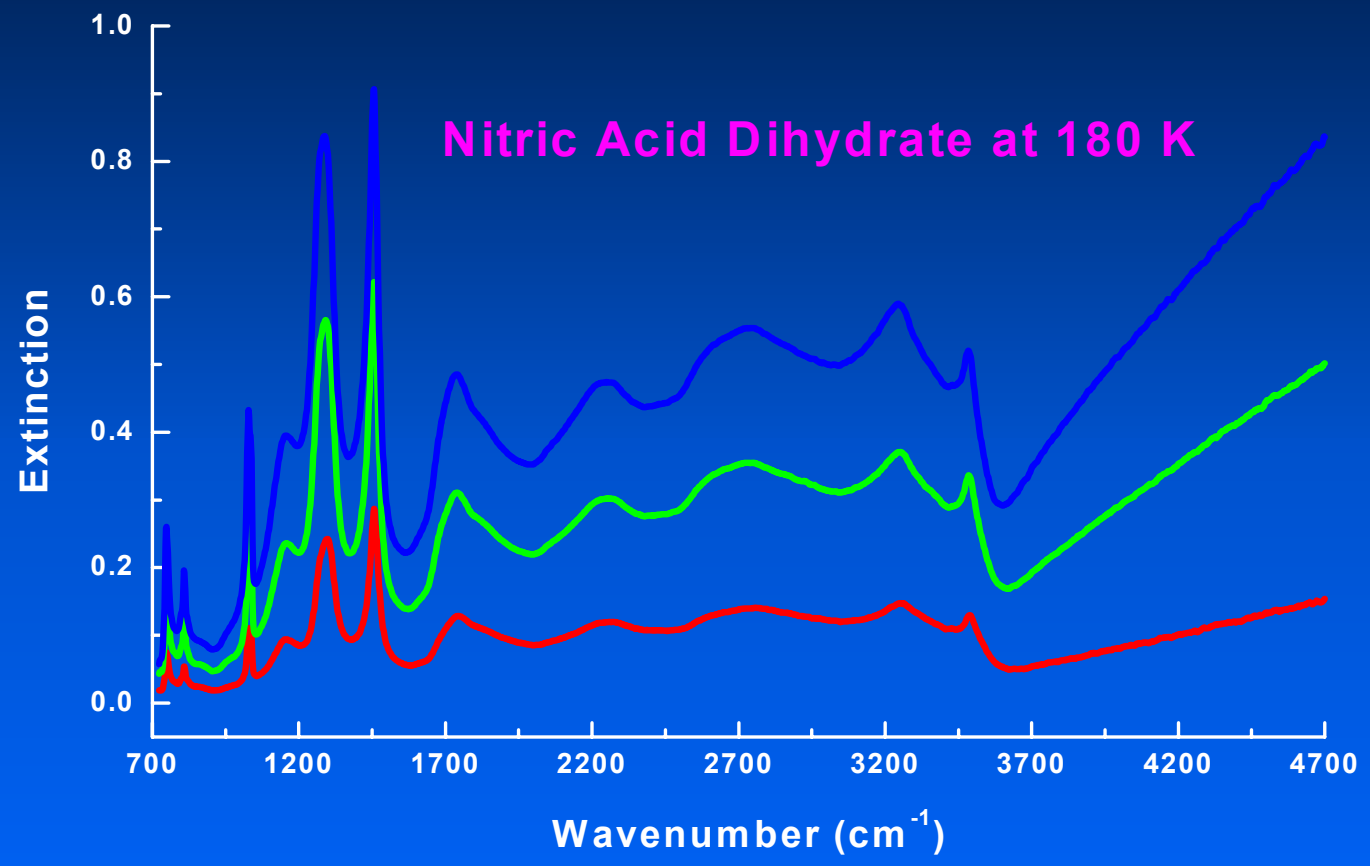
- Different scattering conditions exist for different particle sizes
- Size parameter

$$\alpha = \frac{\pi D}{\lambda}$$

Aerosol Spectroscopy

- $\alpha << 3$
  - Rayleigh scattering
    - "Uniform" electromagnetic field
- $\alpha \approx 3$
  - Mie scattering
    - Electromagnetic field is not uniform over the entire particle
    - Most atmospheric particles fall in this regime
- $\alpha >> 3$
  - Geometric scattering
    - Classical optics

Aerosol Spectroscopy



Aerosol Spectroscopy

- Aerosol extinction spectra can be predicted from Mie scattering theory
  - Spherical particles
  - Particle size information
  - Refractive indices for all relevant materials
  - See texts by Bohren and Huffman (1983), Kerker (1969), and van de Hulst (1957) for details

Aerosol Spectroscopy

- Given an extinction spectrum and a set of refractive indices, one can determine
  - Particle size
  - Particle composition
  - Particle phase
- Assuming the availability of good spectra, characterization depends on the availability of good refractive indices

Refractive Indices

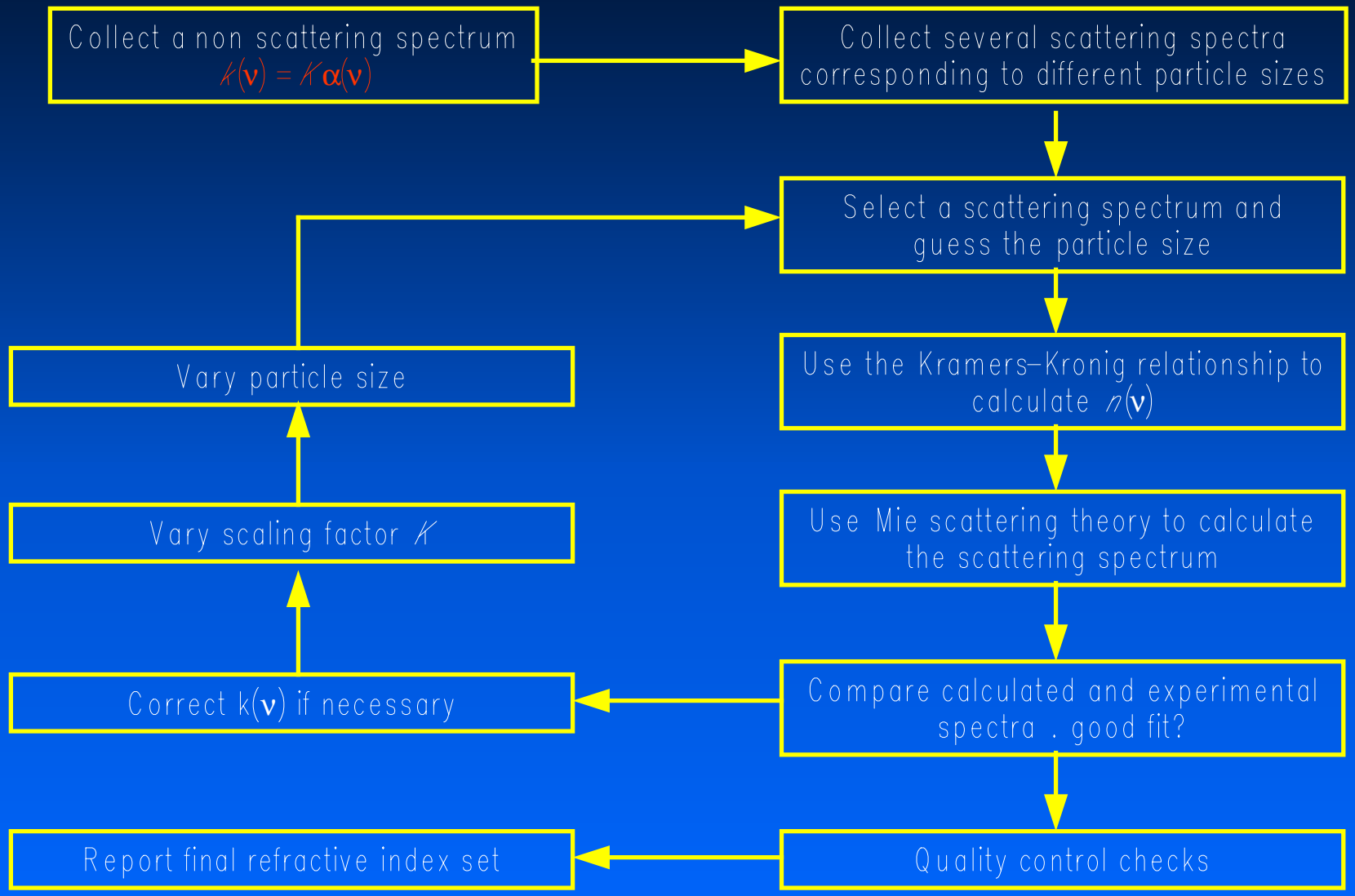
$$N = n + ik$$

- Real index *n* governs scattering
- Imaginary index *k* governs absorption
- Scarce data on refractive indices for most materials relevant to atmospheric studies
  - Not too bad for stratospheric materials
  - Virtually non-existent for tropospheric materials

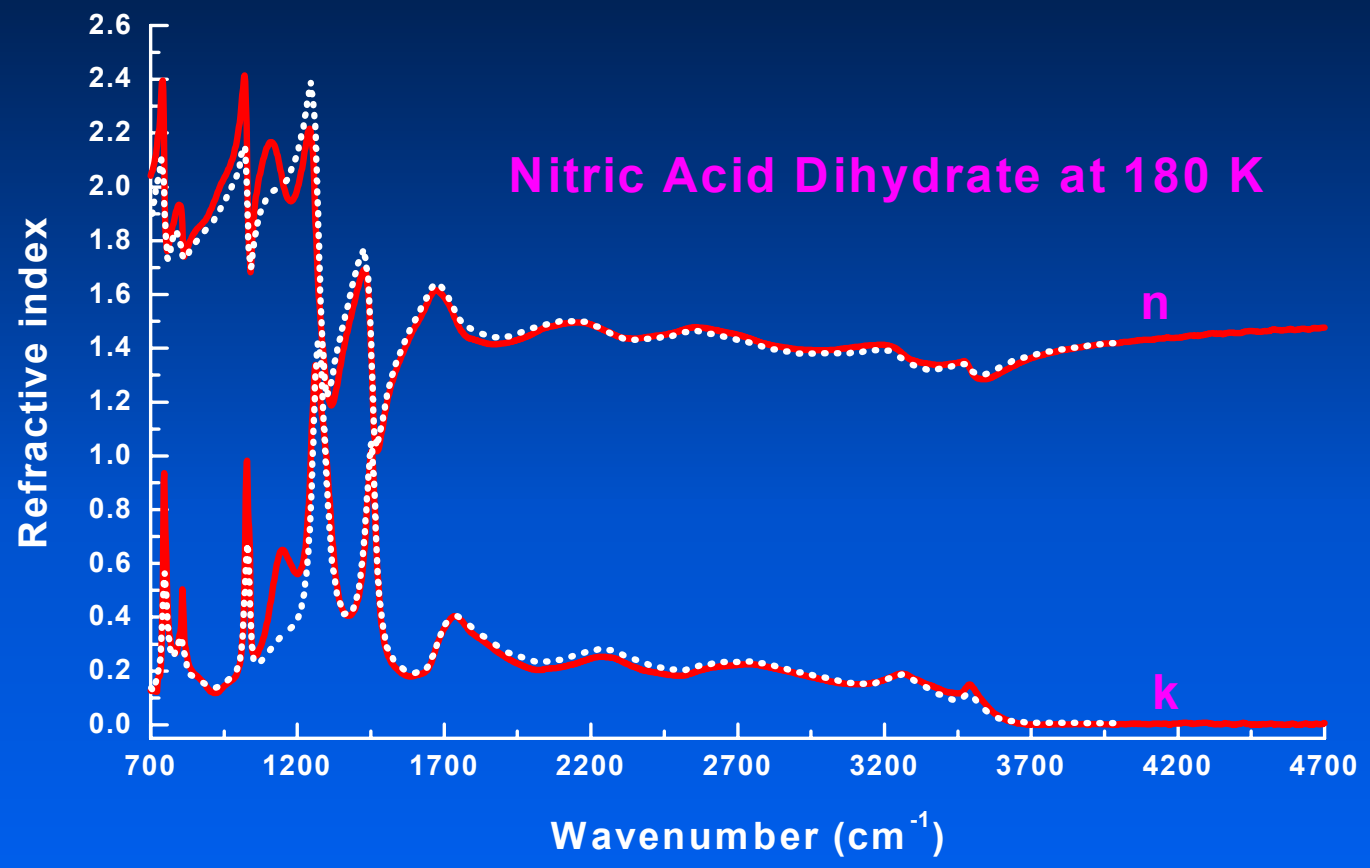
Refractive Indices

- If the lack of refractive index data sets is the problem, what is the solution?
- Measure them!
- Several techniques are available
  - Thin-film spectroscopy
    - Near incidence reflection
    - Transmission
  - Aerosol extinction spectroscopy

Refractive Indices



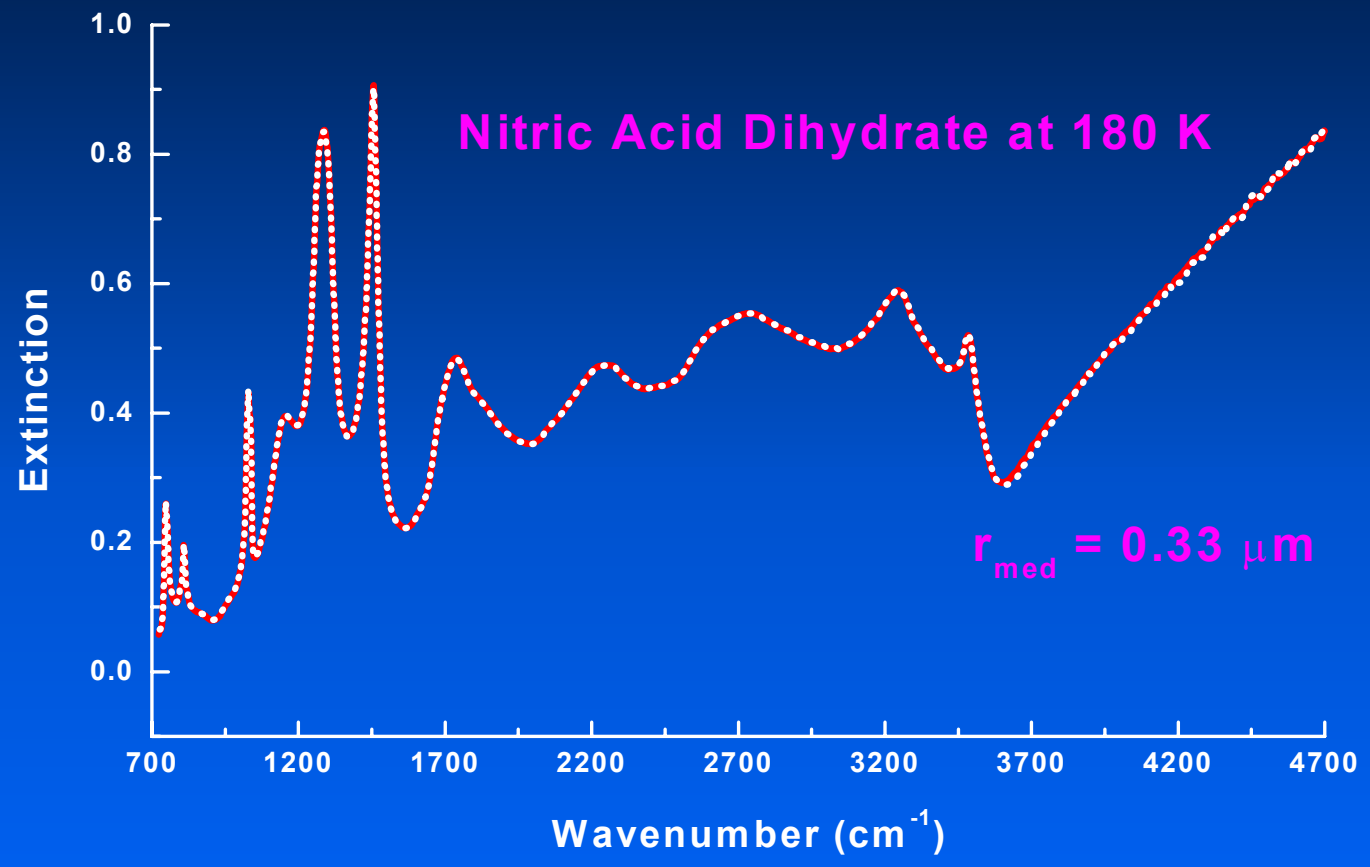
Refractive Indices



Niedziela, *et al.*, *J. Phys. Chem. A*, 102(32), 6477, (1998)

Toon, *et al.*, *J. Geophys. Res.*, 99, 25631, (1994)

Refractive Indices



Refractive Indices

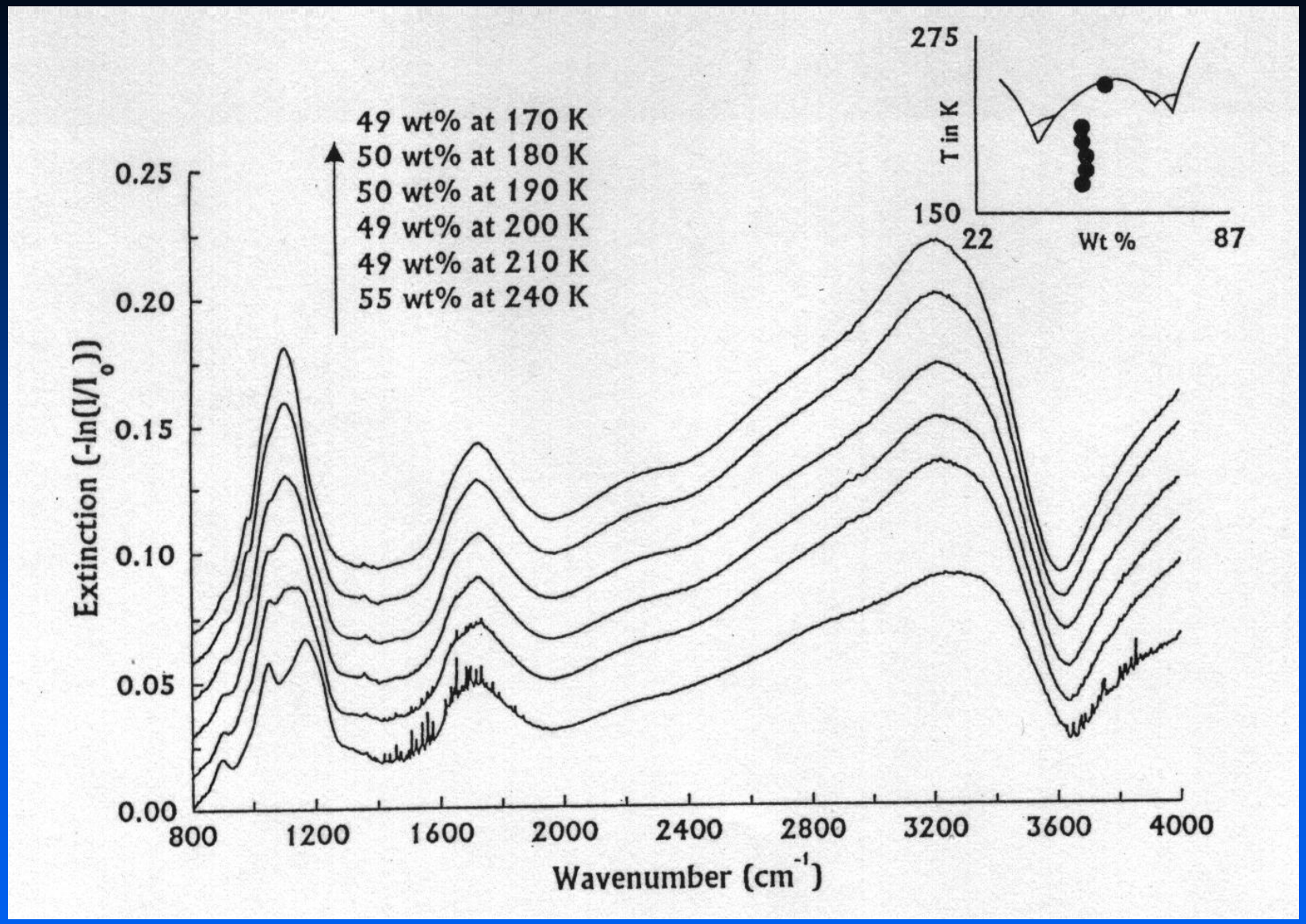
- Available refractive indices for stratospheric aerosols
  - Water ice
    - Warren, *Appl. Opt.*, **23**(8), 1206, (1984)
    - Clapp, *et al.*, *J. Chem. Phys.*, **99**, 6317, (1995)
    - Rajaram, *et al.*, *Appl. Opt.*, **40**(25), 4449, (2001) and references therein
  - Nitric acid dihydrate (NAD)
    - Toon, *et al.*, *J. Geophys. Res.*, **99**, 25631, (1994)
    - Niedziela, *et al.*, *J. Phys. Chem. A*, **102**(32), 6477, (1998)

Refractive Indices

- Available refractive indices for stratospheric aerosols
  - Nitric acid trihydrate (NAT)
    - Richwine, *et al.*, *Geophys. Res. Lett.*, **22**, 2625, (1995)
    - Toon, *et al.*, *J. Geophys. Res.*, **99**, 25631, (1994)

More Complex Systems

- The materials discussed thus far are either pure or have a fixed composition
- This is definitely not true for everything in the atmosphere
- The case of sulfuric acid



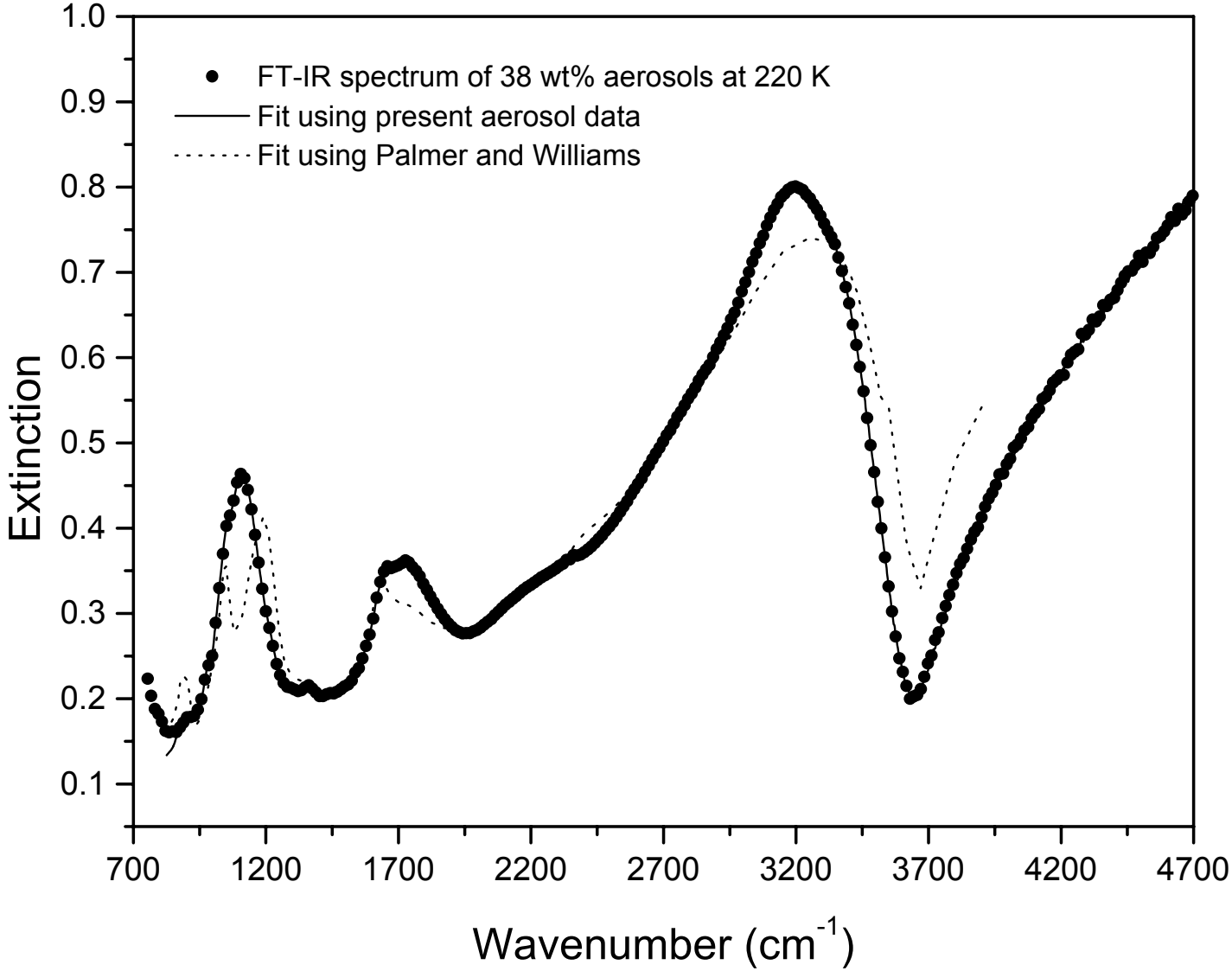
Clapp, *et al.*, *J. Geophys. Res.*, **102**(D7), 8899, (1997)

Sulfuric Acid

- Additional studies on the freezing characteristics of sulfuric acid aerosols have been performed
  - Bertram, *et al.*, *J. Phys. Chem.*, **100**, 2376-2383, (1996)
  - Anthony, *et al.*, *Geophys. Res. Lett.*, **22**, 1105-1108, (1995)
- Studies show that spectra are highly sensitive to temperature and water vapor

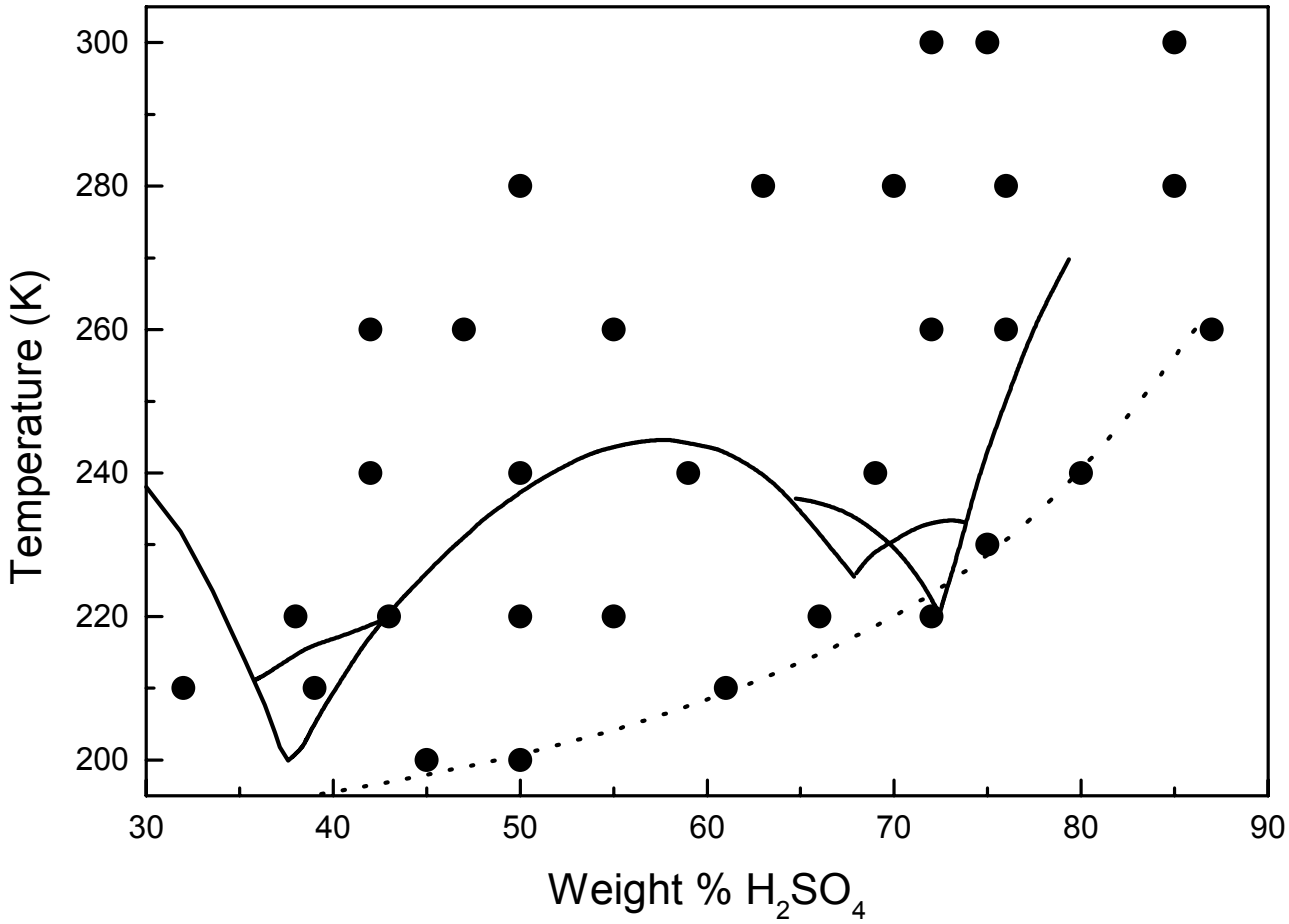
Sulfuric Acid

- Can existing refractive indices be used to model sulfuric acid aerosols?
  - Palmer and Williams, *Appl. Opt.*, **14**, 208-219, (1975)
  - Pinkley and Williams, *J. Opt. Soc. Am.*, **66**, 122-124, (1976)
  - Remsberg, *et al.*, *J. Chem. Eng. Data*, **19**, 263-265, (1974)


FT-IR spectrum of 38 wt% aerosols at 220 K
Fit using present aerosol data
Fit using Palmer and Williams
Extinction
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
700
1200
1700
2200
2700
3200
3700
4200
4700
Wavenumber (cm-1)

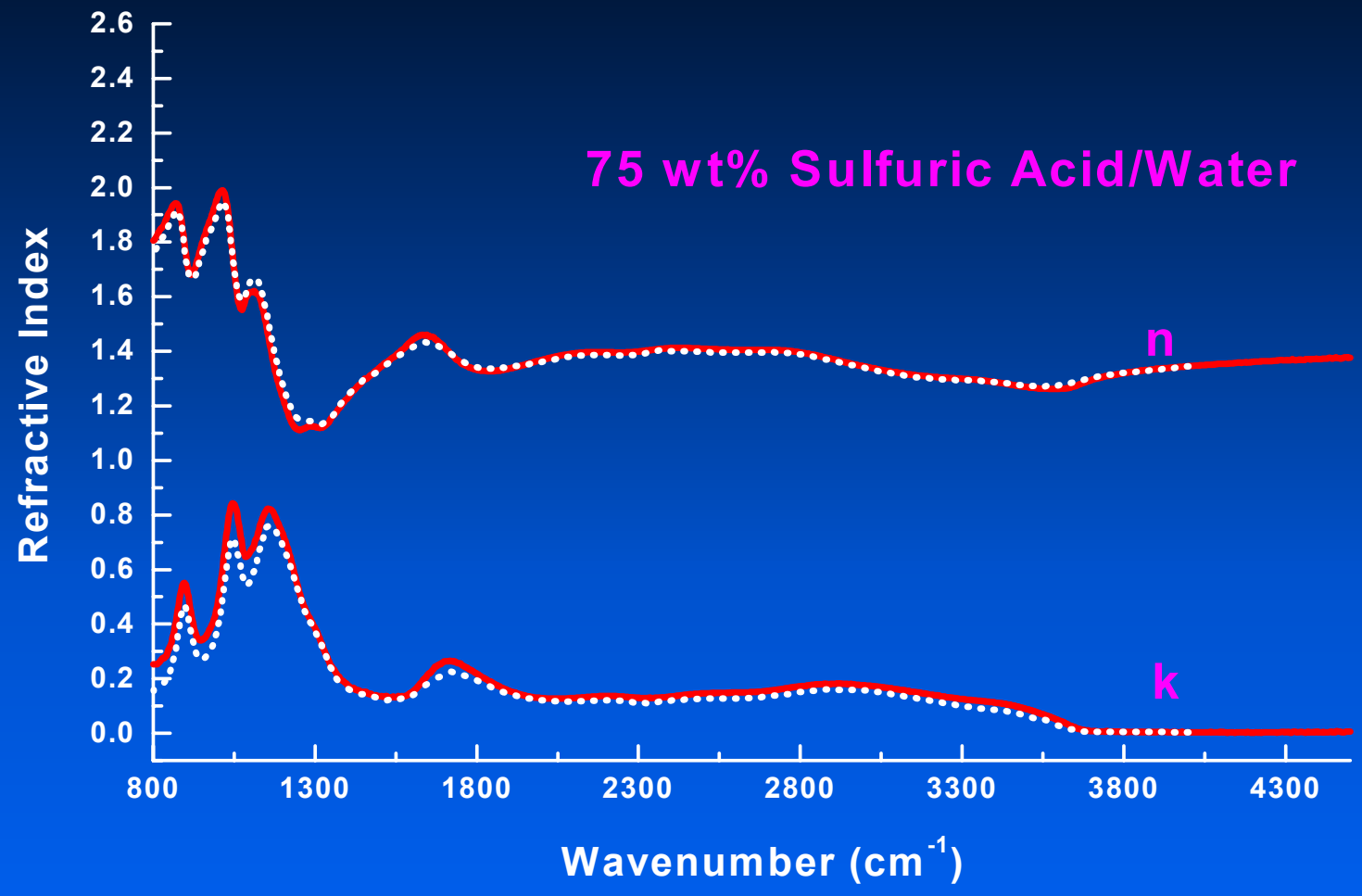
Sulfuric Acid

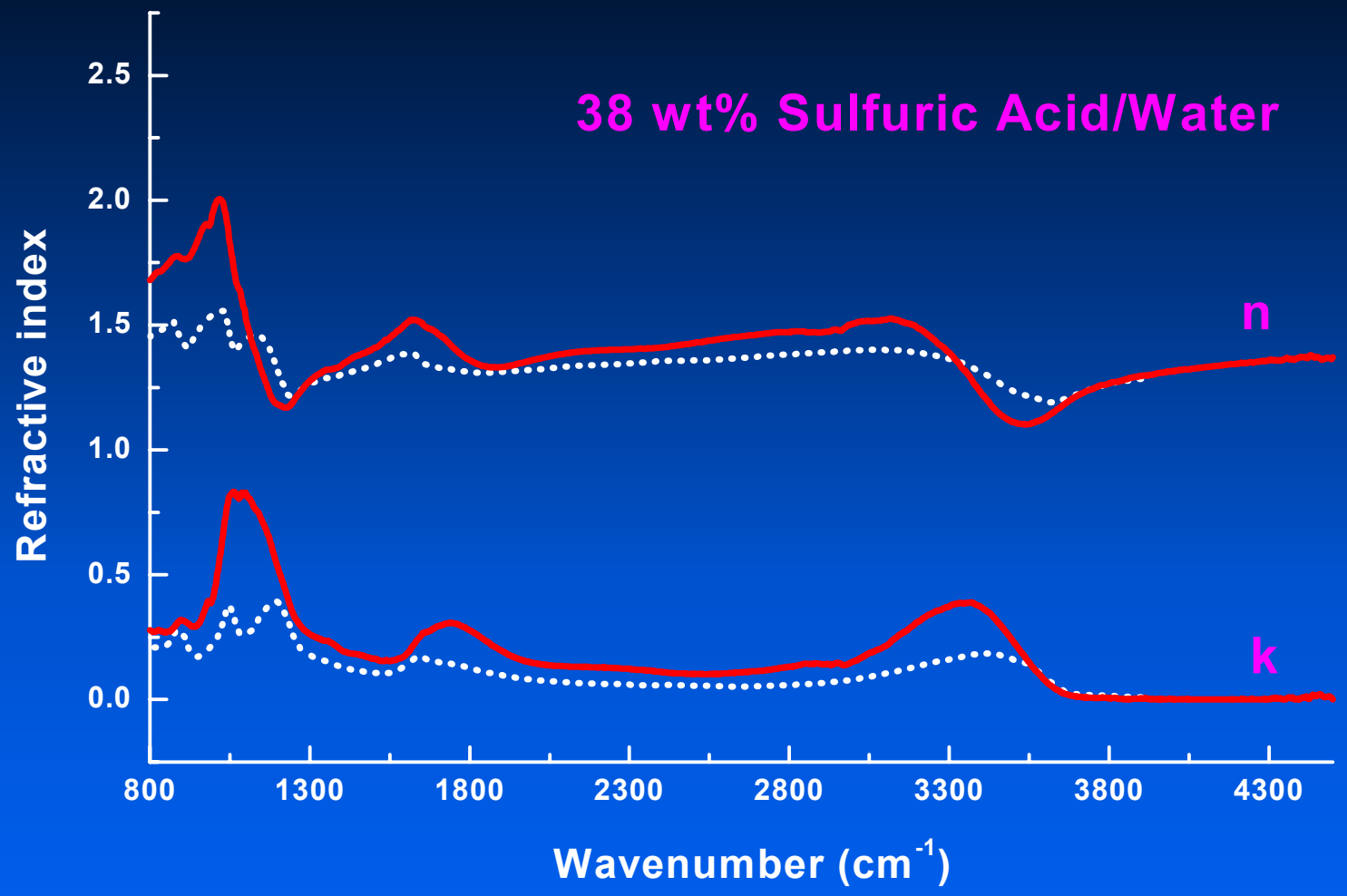
- The answer is no (not entirely)!
- Collect refractive index sets for a number of different sulfuric acid compositions at different temperatures
  - Niedziela, *et al.*, *J. Phys. Chem. A*, **103**(40), 8030-8040, (1999)



Phase diagram: Gable *et al.*, *J. Am. Chem. Soc.*, **72**, 1445–1448, (1950)

Trajectory: Steele and Hamill, *J. Aerosol Sci.*, **12**, 517–528, (1981)


75 wt% Sulfuric Acid/Water
Refractive Index
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
n
k
800
1300
1800
2300
2800
3300
3800
4300
Wavenumber (cm-1)


38 wt% Sulfuric Acid/Water
Refractive index
2.5
2.0
1.5
1.0
0.5
0.0
n
k
800
1300
1800
2300
2800
3300
3800
4300
Wavenumber (cm-1)

Sulfuric Acid

- Composition determination
  - TDL spectroscopy
  - Thermodynamic model of Carslaw, *et al.*, *J. Phys. Chem.*, 99, 11557-11574, (1995)
- Other refractive index data
  - Sulfuric acid at 215 K
    - Tisdale, *et al.*, *J. Geophys. Res.*, **103**(D19), 25353-25370, (1998)

Other Systems

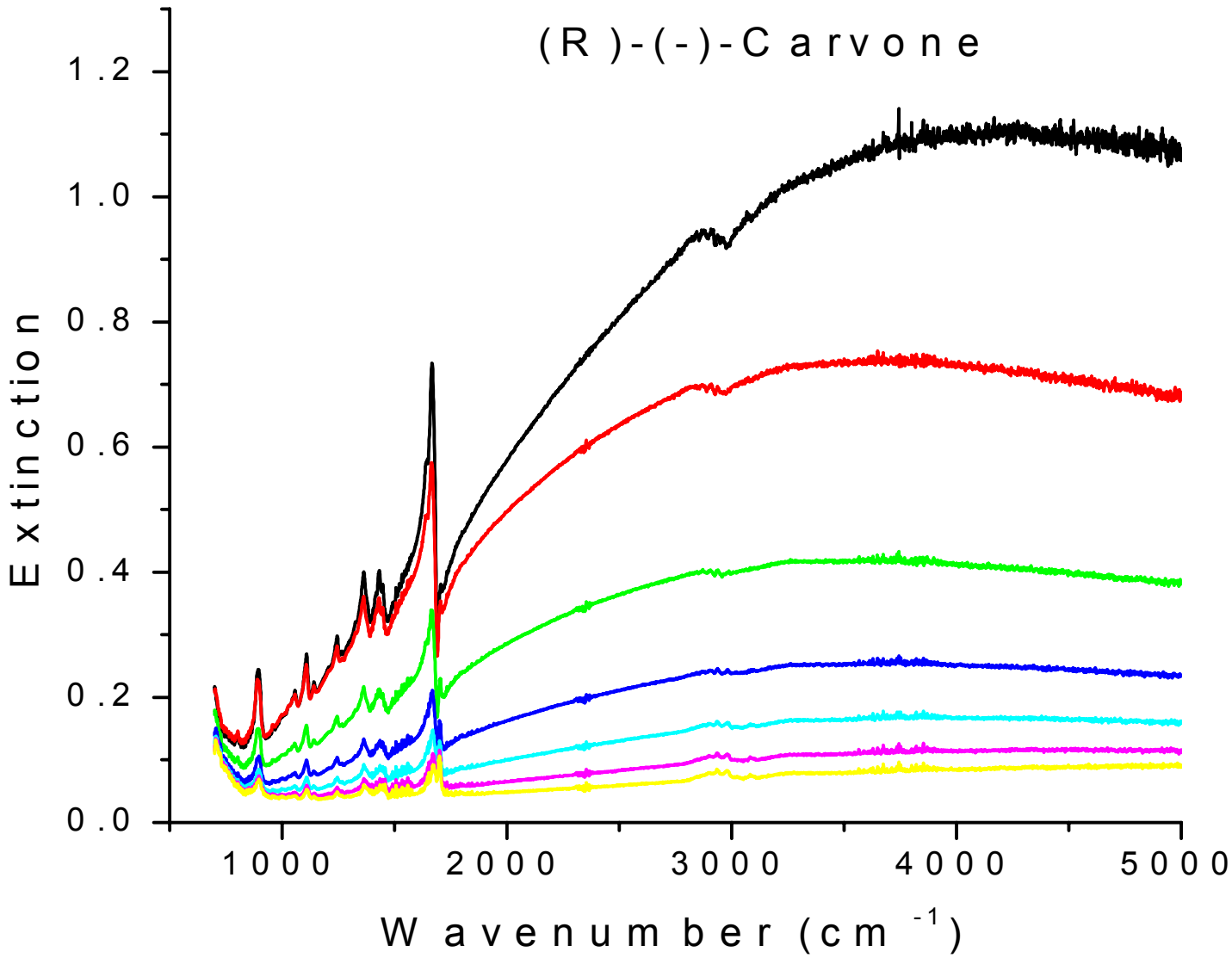
- Ternary systems
  - Biermann, *et al.*, *J. Phys. Chem. A*, **104**, 782-793, (2000)
  - Krieger, *et al.*, *Appl. Opt.*, **39**(21), 3691-3703, (2000)
  - Norman, *et al.*, in preparation, (2001)
- Supercooled nitric acid aerosols
  - Norman, *et al.*, *J. Geophys. Res.*, **104**(D23), 30571-30584, (1999)

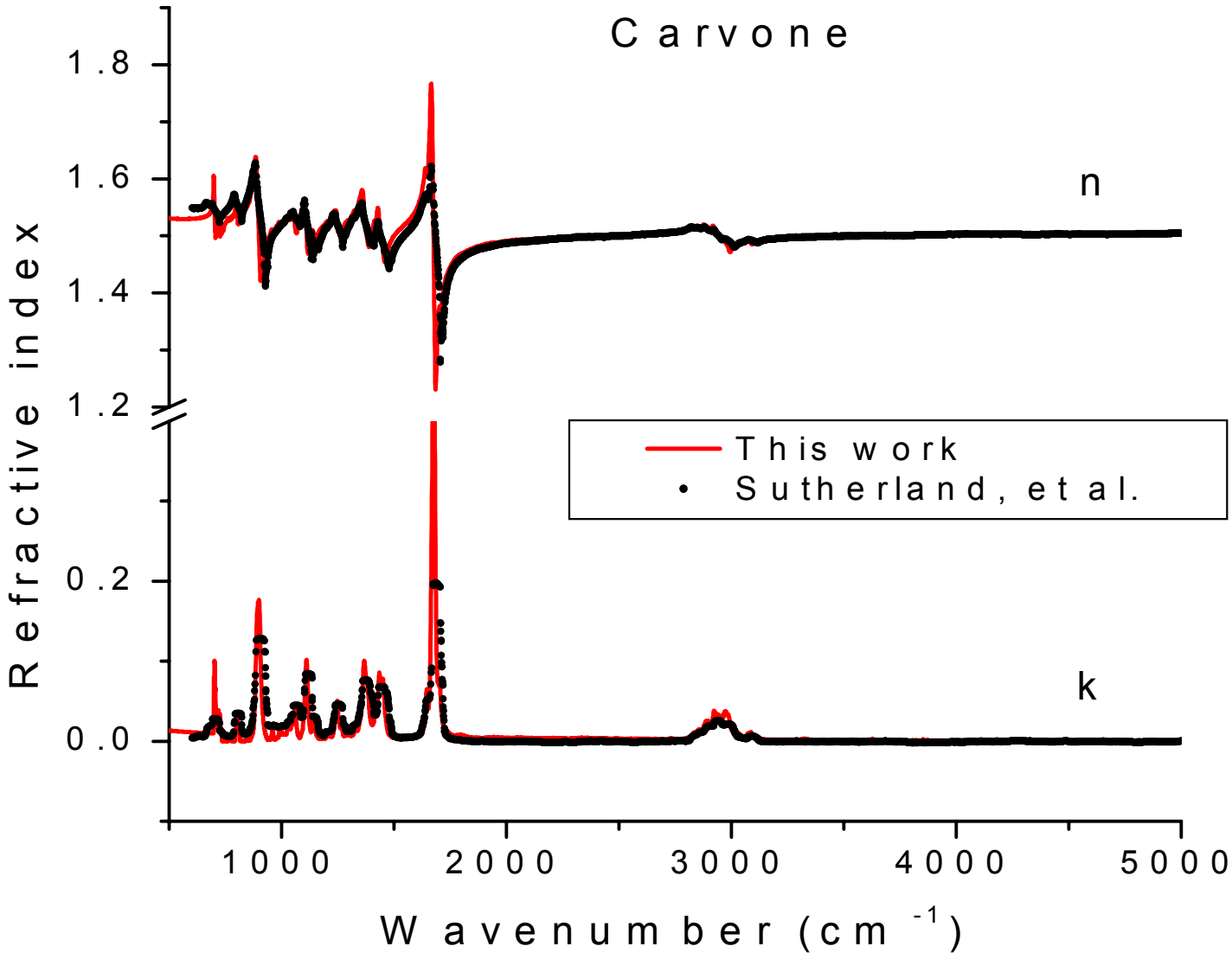
Applications

- Uptake of nitric acid by ice particles
  - Arora, *et al.*, *Geophys. Res. Lett.*, **26**(24), 3621-3624, (1999)
- Supercooling studies of nitric acid aerosols
  - Bertram, *et al.*, *J. Geophys. Res.*, **105**(D7), 9283-9290, (2000)
- Aerosol volume vertical profiles
  - Eldering, *et al.*, *Appl. Opt.*, **40**(18), 3082-3091, (2001)

Organic Systems

- A total lack of refractive index data
- Sutherland, *et al.*, *Aerosol Sci. Tech.*, **20**, 62-70, (1994)
  - 12 sets for terpenes and PAH's
  - Data is lost
- Apply the aerosol refractive index retrieval technique to organic systems


(R)-(-)-Carvone
Extinction
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1000
2000
3000
4000
5000
Wavenumber (cm -1)

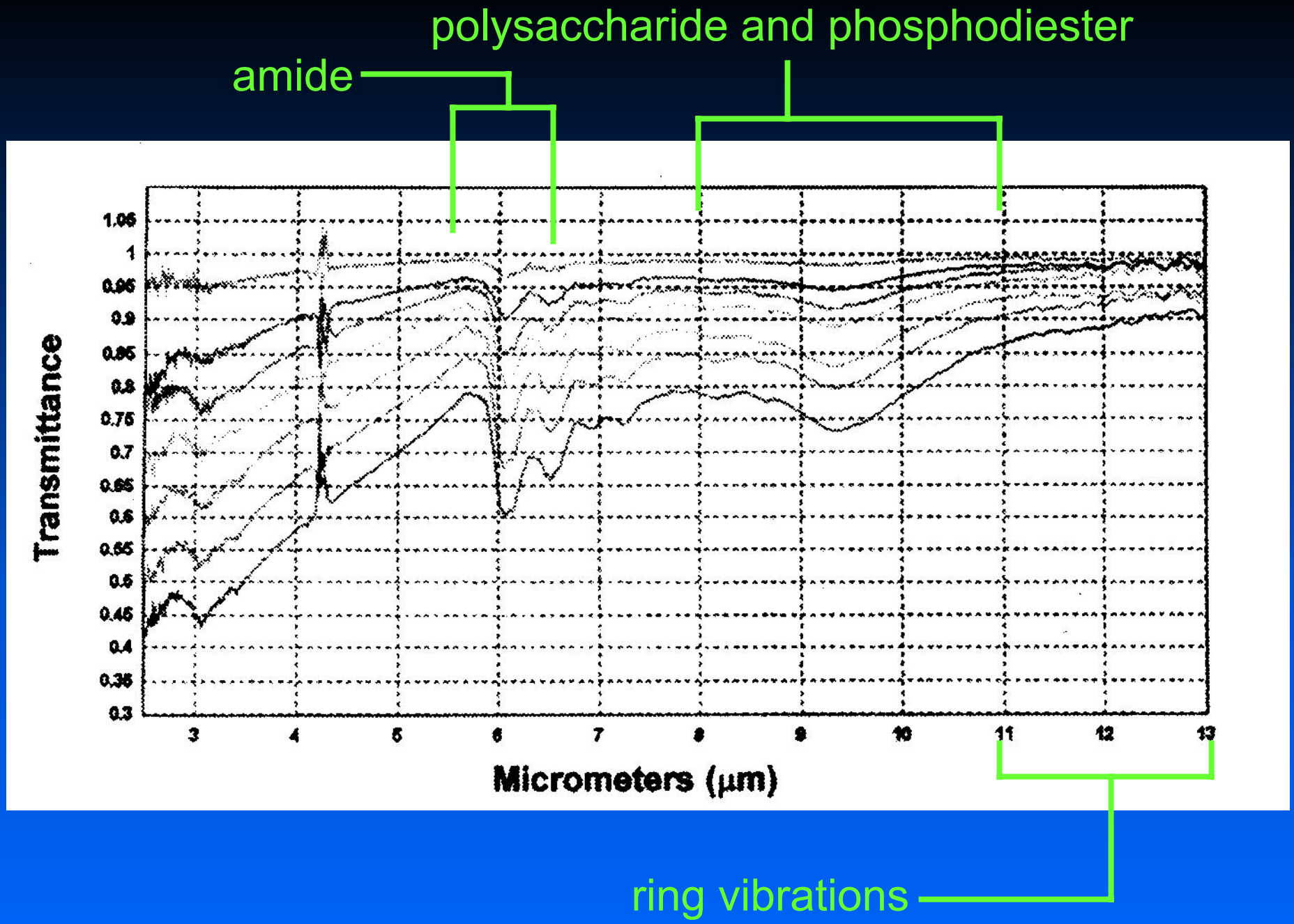

Carvone
1.8
1.6
1.4
1.2
0.2
0.0
Refractive index
n
k
This work
Sutherland, et al.
1000
2000
3000
4000
5000
Wavenumber (cm -1)

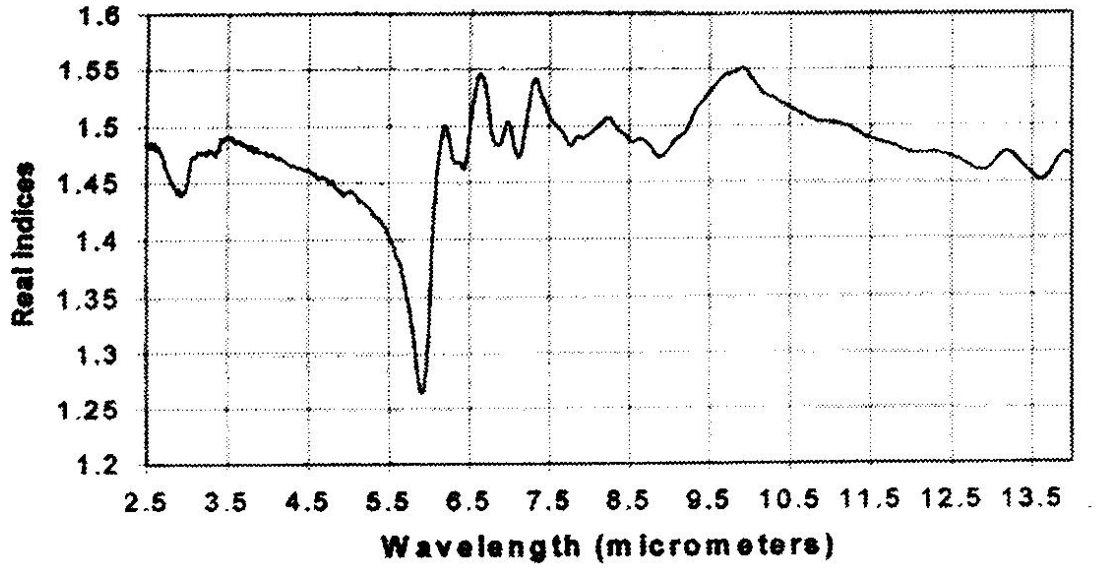
Detection of Biomaterials

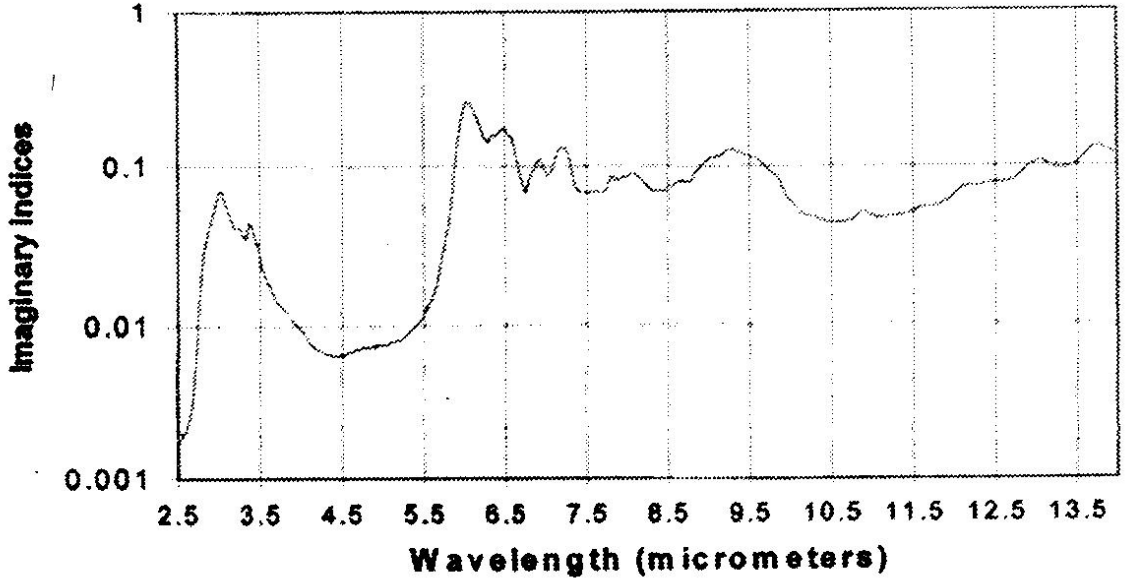
- Is it possible to use spectroscopic methods to detect airborne bacteria?
- Advanced warning at safe distances
- As with other remote sensing applications, optical properties are needed

Detection of Biomaterials

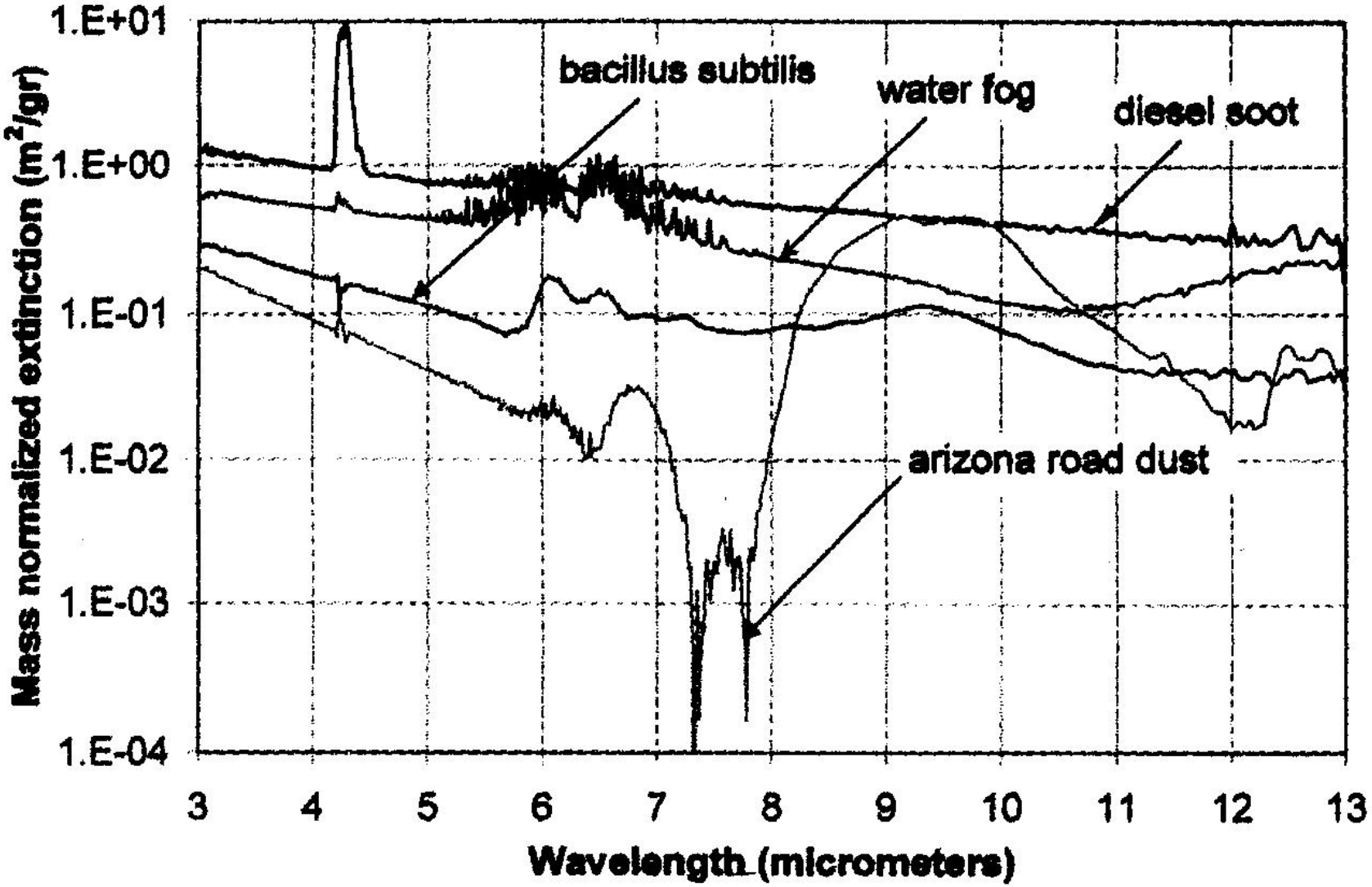
- What assumptions can we make?
  - Solid geometry (e.g., spherical or not)
  - Homogeneity
  - Refractive indices
- IR spectral extinction of *bacillus subtilis* var. *niger*
  - K.P. Gurton, D. Ligon, and R. Kvavilashvili, *Appl. Opt.*, **40**(25), 4443, (2001)


polysaccharide and phosphodiester
amide
ring vibrations
Transmittance
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
3
4
5
6
7
8
9
10
11
12
13
Micrometers (μm)





From Milham and Querry (unpublished). See D.F. Flannigan, Tech. Rep. ERDEC-TR-416 (Edgewood Research, Development, and Engineering Center, Aberdeen Proving Ground, Aberdeen, MD 1997), Appendix B


1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
Mass normalized extinction (m²/gr)
bacillus subtilis
water fog
diesel soot
arizona road dust
3
4
5
6
7
8
9
10
11
12
13
Wavelength (micrometers)

Summary

- Aerosol spectroscopy can be used for many applications
  - From particle sizing…
  - … to refractive index retrievals
- Future focus
  - Tropospheric aerosols
    - Multi-component systems
    - How far can we extend spectroscopic techniques?

Acknowledgments

- NASA UARP Grant NAG5-3946
- DePaul University Faculty Summer Research and Development Grants (1999 and 2001)
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- UNC
  - Roger Miller and Mark Norman
- DPU
  - Allison Potscavage