Lecture 21: Instrumentation

Required reading: FP&P Chapter 11

Atmospheric Chemistry
CHEM-5151/ATOC-5151
Spring 2005
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Outline of Lecture

- Intro
- Gases
  - Collection Techniques
    - Filters and Denuders
  - Spectroscopic Techniques
    - Absorbance vs. Emission
    - Measuring OH
- Particles
  - Collection Techniques
  - Mass Spectrometry Techniques
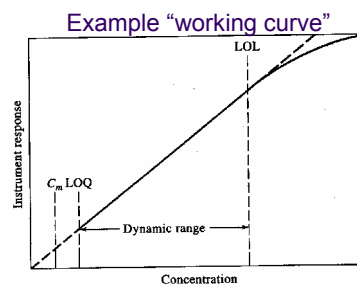   - Bulk, Single-particle, Morphology

Introduction

- Measuring atmospheric constituents presents many challenges:
  - Identify and quantify
  - Complex system
    - Large number of possible interferences
  - Very small concentrations
    - Sub ppt
  - Concentrations vary!
    - Diurnally, temporally, geographically, etc.

Introduction

- Many different ways to measure/analyze
  - Which technique is the best?
  - How well do different techniques compare?
- Instrumentation requirements:
  - Exceptional sensitivity
  - Low limit of detection
  - Good selectivity
  - Good time resolution
  - Accurate and reproducible
  - Robust, portable, cheap, …

Example "working curve"

LOL

C_m LOQ

Dynamic range

Instrument response

Concentration

From Skoog, Holler, Nieman
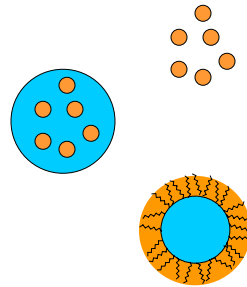
Important Distinctions

- Many measurement techniques will fall into one or more of these important categories:

  - Gas-phase vs. Particles

    - Particles:
      - Bulk analysis
      - Single-particle analysis
      - Depth Profiling/Morphology

  - Collected vs. In situ

Gas-phase

Collection Techniques

- Collect gases for subsequent analysis
  - Must avoid interferences from particles
- Must collect enough to be measurable
  - Sampling times are usually quite long (min to day)
  - Be careful of time resolution of measurements
    - From total volume of air sampled and the amount of the analyte measured, the average concentration of the species over experimental time range is determined
- Beware of sampling artifacts
  - Reaction, decomposition, evaporation, etc.

Collection Techniques

- Filters
  - Saturated with a substance that takes up the species of interest
    - Filter material is optimized for the compound of interest
    - Nylon is good for HNO_3 (*g*)

  - Analytes are later extracted from filter prior to analysis
  - Performance of filter must be carefully assessed prior to use

Impregnated Whatman 41 filter for NH3 — Nylon for HNO3 — Teflon 1μm pore size for particles — Air flow — Teflon
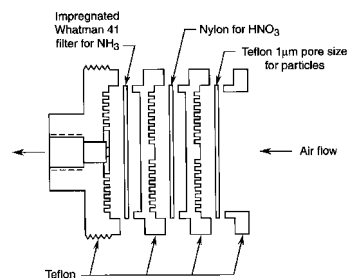
FIGURE 11.22 Schematic diagram of a typical filter pack used to measure gaseous HNO_3, particulate matter, and gaseous NH_3 (adapted from Anlauf *et al.*, 1988). *Finlayson-Pitts*

1. Remove particles
2. Collect HNO_3 (*g*)
3. Collect NH_3 (*g*)
4. Everything else goes thru

Collection Techniques

- Denuders
  - Special kind of filter that uses diffusion properties to separate gas and particles
    - Gases strike wall of tube numerous times because of their high diffusivity, particles just fly through
  - Walls of tube are coated with a substance that takes up only the species of interest
 - "Wash" the walls to collect the gas prior to analysis

Absorptive coating
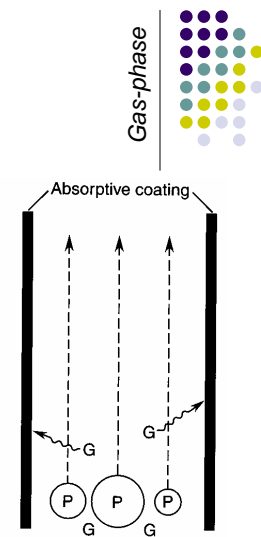
Schematic diagram of a denuder. G=gas and P=particles

Finlayson-Pitts


Review of Spectroscopy

- Identify and quantify species based on their interactions with energy
  - Energy: **radiation**, acoustic waves, beams of particles such as ions and electrons
- The energy difference b/w states is unique for every species!
- Quantum theory:
  - Atoms, ions, and molecules exist in discrete states, characterized by definite amounts of **E**
  - When a species changes its state, it absorbs or emits an amount of energy *exactly* equal to the energy difference between states, **E=$h\Delta v$**

E_2

E_1

Energy

E_o

Review of Spectroscopy

Gas-phase
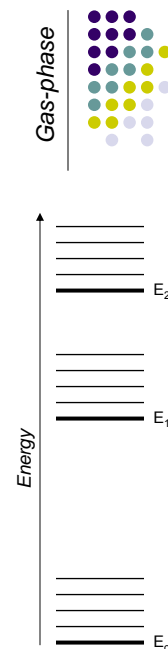
- Absorbance:
  - Select frequencies are removed from the incident light by absorption.
  - Absorption promotes molecules from ground state to an excited state.
  - Analytical techniques: IR and UV-VIS
- Emission:
  - Select frequencies are emitted when excited molecules return to ground state
  - Initial excitation occurs by irradiation or rxn
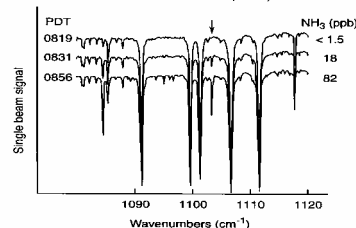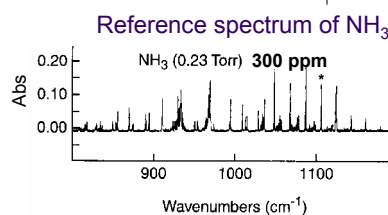 - Analytical techniques: Fluorescence and Chemiluminescence

E_2

E_1

Energy

E_o

Absorbance-Based Techniques

Gas-phase
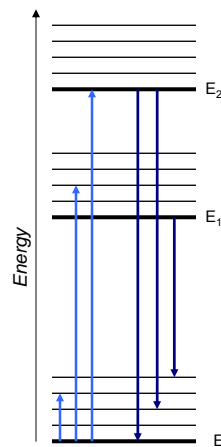
- Challenges:
  - Every molecule has an absorption spectrum of some sort
  - It is difficult to separate contributions to absorbance from different molecules

$$Abs = \ln(I_0/I) = \Sigma(\sigma_i \times L \times n_i) \quad i = 1,2,3,\ldots$$

  - Useful only for analysis of molecules with *structured* absorbance spectra
    - See NH_3 example

Reference spectrum of NH_3

Abs

NH_3 (0.23 Torr) **300 ppm**

0.20

0.10

0.00

900   1000   1100

Wavenumbers (cm^{-1})

PDT NH_3 (ppb)

0819   < 1.5

0831   18

0856   82

Single beam signal

1090   1100   1110   1120

Wavenumbers (cm^{-1})

Typical FT-IR spectra in ambient air as a function of time in the NH_3 region.

See FP&P Figures 11.4b and 11.3

Absorbance-Based Techniques

- Infrared absorption spectroscopy
  - Most molecules have highly structured and unique IR spectra – "fingerprints"
  - Absorption cross sections are generally small
    - Multipass cells, FTIR, TDLS, and NDIR
  - Large portion of the IR range is dominated by H_2O, CO_2 and CH_4
- UV/VIS absorption spectroscopy
  - Fewer molecules have structured UV spectra
    - NO_2, H_2CO, HONO, etc
  - Absorption cross sections are generally large
  - Large continuous Rayleigh scattering and background absorption by O_3, certain organics, etc.
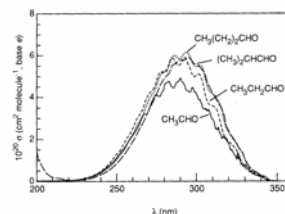
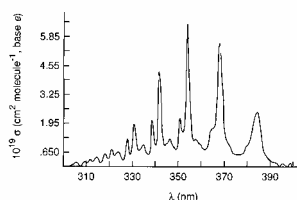FIGURE 4.27 Absorption spectra for some simple aldehydes (adapted from Martinez *et al.*, 1992).

FIGURE 4.14 Absorption spectrum of HONO at 277 K (adapted from Bongartz *et al.*, 1991). Note that the absolute values of the cross sections shown here should be multiplied by 0.855 as recommended by Bongartz *et al.* (1994).
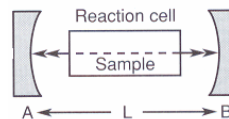

Absorbance-Based Techniques

- Direct absorption spectroscopy:
  - $A = \ln(I_o/I) = \sigma\, L\, N$
  - Longer pathlength $\Longrightarrow$ Higher sensitivity
    - Mulitpath cells:
      - Pathlength = 0.5 – 100 m
      - Lose power due to mirrors
    - Cavity based methods:
      - Pathlength = 1 – 10 km
      - Expensive mirrors and pulsed laser
    - Long distance measurements:
      - Pathlength = 100 m – 1 km
      - In situ measurements
      - Poor spatial resolution
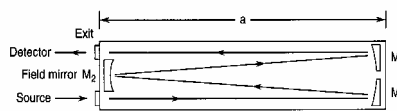
Multipass White cell. *FP&P*

Cavity ring down cell. *FP&P*

Absorbance-Based Techniques: DOAS

- Differential Optical Absorption Spectroscopy
  - Used to measure concentrations of trace gases by measuring their specific narrow band absorption structures
    - Technique was specifically invented for molecules which have highly structured absorption spectra in the UV/VIS
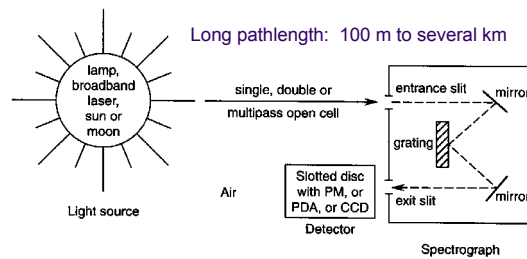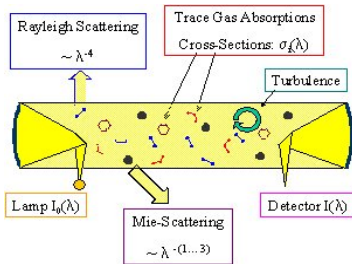   - Corrects for background absorption

Long pathlength: 100 m to several km

FIGURE 11.11 Schematic diagram of components of a DOAS system. *Finlayson-Pitts*
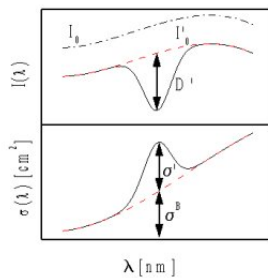

Absorbance-Based Techniques: DOAS

From Jochen Stutz (UCLA)

$$I(\lambda) = I_o(\lambda) \exp -[\Sigma\ \sigma_i(\lambda) \times N_i \times L + \sigma_{ray}(\lambda) + \sigma_{mie}(\lambda)]$$

- $I_o(\lambda)$ under goes extinction by air molecules (σ_{ray}), aerosols (σ_{mie}), and absorption by gases (σ_i)
- Need to separate these effects in order to derive concentration, N
- DOAS treats the slow-varying continuous background under the structured spectrum as an effective baseline
  - $\sigma_i(\lambda) = \sigma^B(\lambda) + \sigma'(\lambda)$
    - $\sigma^B(\lambda)$ = background (broad, low-frequency)
    - $\sigma'(\lambda)$ = effective cross section (high frequency)
- Uses the effective cross sections to convert the differential absorbance into concentration
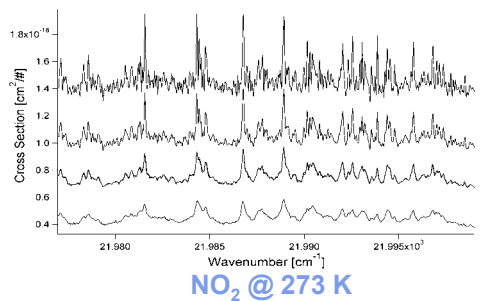 - **Differential Absorbance = ln(I_o'/I) = $\sigma' \times L \times N$**

Absorbance-Based Techniques: DOAS

- Advantages
  - High sensitivity for species with narrow bands in the UV-Vis
  - Multipule compounds can be monitored simultaneously
  - Real-time measurements, no air sample collection required
  - Differential optical coefficients are fundamental spectroscopic properties
    - No field calibrations are required

- Disadvantages
  - Large background can push the Beer-Lambert law into the non-linear regime
  - High-res structure in the absorption spectra of certain molecules is strongly pressure and temperature dependent.

NO$_2$ @ 273 K

Absorbance-Based Techniques: Dobson Spec.

From http://ozone.gi.alaska.edu/dobson.htm

Inside a Dobson Spectrophotometer

An R-dial moves the filter wedge until the two light intensities are equal
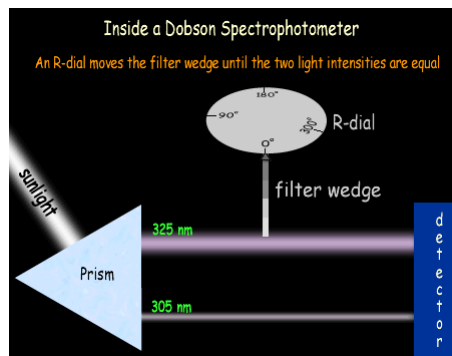
- Measure [O$_3$]
  - UV light at 2+ wavelengths from 305-345 nm
  - One λ is absorbed strongly by O$_3$ (305 nm) the other λ is not absorbed (325 nm)
  - The ratio b/w the two light intensities is a measure of the amount of O$_3$ in the light path from the sun to the detector

- Gradually move the filter wedge by turning the R-dial, so that the intensity of the 325 nm and 305 nm light are equal.
- By taking the R-dial reading with the intensities of the two wavelengths are equal, light intensity ratio is determined

Emission-Based Techniques

- **Chemiluminescence:** detect photons emitted by electronically excited products of a reaction

$$O_3 + NO \rightarrow NO_2^* + O_2$$
$$NO_2^* \rightarrow NO_2 + hv \qquad (hv \text{ is detected})$$

- For detection of NO, add excess O_3 to the air stream.
- This reaction can be used to detect either O_3 or NO.

- **Fluorescence:** detect photons emitted by molecules excited with a laser or UV-lamp

$$SO_2 + hv \rightarrow SO_2^*$$
$$SO_2^* \rightarrow SO_2 + hv' \qquad (hv' \text{ is detected, normally } hv' < hv)$$

- NO, SO_2, NO_2 are some of the molecules that have large fluorescence quantum yields.

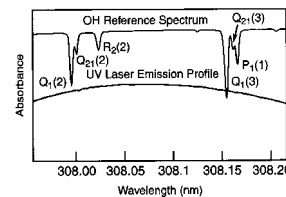# Measuring OH

- **DOAS** (Absorption)
  - OH undergoes an allowed transition b/w its ground state and first electronically excited state
    - Result is a characteristic banded absorption structure around 308 nm
  - Absorption cross sections for OH are well known, so absolute [OH] can be calculated based solely on the absorption spectra

- **LIF** (Emission = fluorescence)
  - Uses the same electronic transition as DOAS
    - Excite with λ = 282 (v' = 1) or **308 nm** (v' = 0)
    - Fluorescence is in competition w/ deactivation
  - Artifact formation of OH can occur during measurements

A typical broadband laser emission profile, and an OH reference spectrum with absorption lines shown.
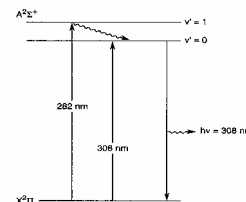
FIGURE 11.43 Schematic diagram of OH energy levels used in LIF measurements.

From Finlayson-Pitts

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Measuring OH

- Both techniques directly measure OH
  - OH is highly reactive and in very low concentrations
    - DOAS LOD_{OH} = 1.5×10^6 cm^{-3}
    - LIF LOD_{OH} = 5×10^6 cm^{-3}
  - Unrecognized OH sources may have affected the long-path DOAS measurements more than the point measurements made by LIF

  - Other indirect techniques:
    - Mass balance approach
    - Mass spectrometry
    - Radiocarbon methods

From Finlayson-Pitts
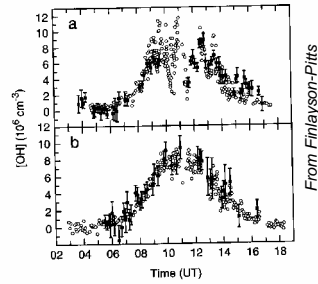
FIGURE 11.49 Diurnal variation of OH measured using LIF (○) and DOAS (●) in a rural area in Germany on the (a) 16th and (b) 17th of August 1994. (Adapted from Hofzumahaus et al., 1998.)

From Finlayson-Pitts

FIGURE 11.50 Correlation between OH measurements made by DOAS and by LIF in a rural area in Germany in August 1994. The data indicated by asterisks were measurements made when the wind was from a particular direction suggesting it might contain unrecognized OH sources affecting the long-path DOAS measurements (adapted from Hofzumahaus et al., 1998).

Particles

11

Particles

- Chemical composition and size distribution is important
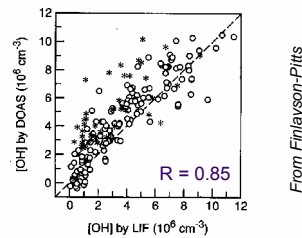 - Bulk analysis: collect particles and analyze them for their mass content and average chemical composition
  - Wide range of sizes: ultrafine to coarse
  - Complex compositions: elemental/organic/inorganic
- Significant variations in chemical composition b/w particles even within the same size range
  - Measure size-resolved properties in real time!
  - Single-particle in-situ analysis techniques are growing
- **Goals:**
  - Elucidate particle sources, the atmospheric chemistry of particles, and the processes involved in their formation, evolution, and ultimate fate, in addition to their impacts on health and climate

Sampling and Collection

- Obtain a representative sample over the desired size range and separate the particles from the air
  - Humidity, temperature, and particle concentration should be controlled during sampling to maintain sample integrity
- Extract particles from the air via filtration
  - Examples: sedimentation, inertial impaction, diffusion, and electrostatic precipitation
  - Almost any kind of filter will fail to catch particles outside a certain size range
    - No "one size fits all" filter

Sampling and Collection

- Beware of sampling artifacts:
  - You want to remove the gaseous species, but there is an equilibrium between the gas-phase and the particle-phase especially for aerosols containing semi-volatile compounds

    Equilibrium: *Gas Phase* ⟷ *Particle Phase*

- Goal
  - To collect atmospheric aerosols without biasing the measurements of the compounds' gas/particle ratio
    - Positive artifact: Increased P because G not removed
    - Negative artifact: Desorption from P b/c all G removed

Sampling and Collection

- Denuder-Filter Samplers
  - Denuders remove the gas from the sample air-stream before particle filter collection.
  - Correct for negative bias
    - Equilibrium shifts from particle to gas phase as particles travel through denuder
    - Volatile compounds will evaporate from collected particles downstream of denuder
    - Use a backup filter to correct for this
  - Advantages:
    - Good flow rates (2-100's of Lpm)
    - Can use shorter collection times
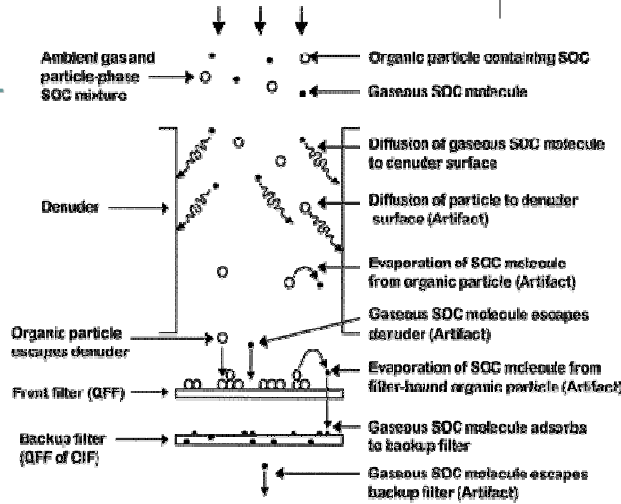
Sampling and Collection

Important processes occurring in a denuder-filter sampler

SOC
Semi-volatile organic carbon

QFF
Quartz fiber filter

CIF
Carbon-impregnated cellulose filter

Ambient gas and particle-phase SOC mixture

Organic particle containing SOC

Gaseous SOC molecule

Diffusion of gaseous SOC molecule to denuder surface

Denuder

Diffusion of particle to denuder surface (Artifact)

Evaporation of SOC molecule from organic particle (Artifact)

Organic particle escapes denuder

Gaseous SOC molecule escapes denuder (Artifact)

Front filter (QFF)

Evaporation of SOC molecule from filter-bound organic particle (Artifact)

Backup filter (QFF of CIF)

Gaseous SOC molecule adsorbs to backup filter

Gaseous SOC molecule escapes backup filter (Artifact)

From Mader et al. 2001. Environ. Sci. Tech. 35, 4857.

Physical Characteristics of Particles: Mass

- Total mass per unit volume of air
  - A major parameter used to characterize particles
 - Basis of air quality standards for particulate matter

$PM_{2.5} = 45 \ \mu g \ m^{-3}$ **Pittsburgh** $PM_{2.5} = 4 \ \mu g \ m^{-3}$
July 2, 2001   July 18, 2001

From Qi Zhang

Pictures taken from a same location at same time of day, on two different days

- Measured by gravimetric methods, β-ray attenuation, piezoelectric and oscillating microbalances

Physical Characteristics of Particles: Size Dist.

- Particle size distribution
    - Harder to measure compared to mass
    - Not all particles are spherical or simple in shape
    - Size range covers ~ 5 orders of magnitude
- Deposited particles:
    - Electron / optical microscopy requires visual examination of particles deposited on a substrate
        - Examples: TEM, SEM, AFM, EDS
- Suspended particles:
    - Light scattering. As larger particles scatter more light one can measure their size distribution using optical detection.
    - Mobility analyzers rely on the fact that larger charged particles experience more resistance when they are dragged through gas in an electrostatic field.
    - Time-of-Flight methods measure sizes of individual particles from their velocity acquired after a controlled acceleration (e.g., expansion through a supersonic nozzle)

MODEL 3081 LONG DMA
Sheath air in
Polydisperse aerosol in
High-voltage rod
Excess air out
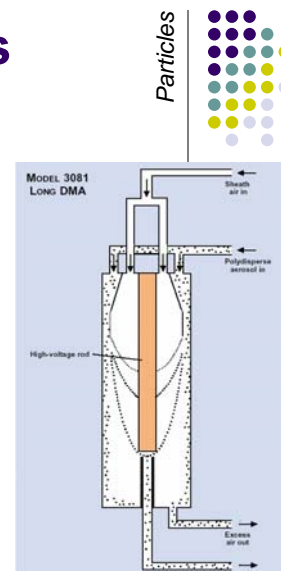
Differential Mobility Analyzer made by TSI http://www.tsi.com/ (currently monopolists in aerosol instrumentations)

Chemical Composition of Particles

- Mass-Spectrometric Techniques
    - Highly adaptable
        - Gas, liquid, and solid phase samples
        - Elements to complex molecules
        - Organic and inorganic species
    - Lots of information
        - Elemental composition to molecular weight
        - Functional groups to complete structure
    - Highly sensitive technique
    - Disadvantages:
        - Many require extensive sample preparation
        - Sample is destroyed
        - Requires vacuum

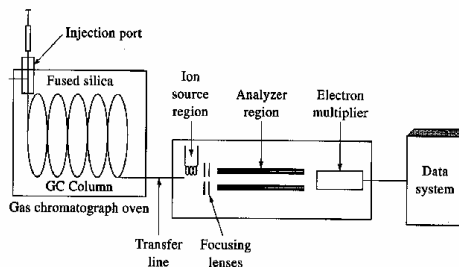# Chemical Composition of Particles

- Mass spectrometer components
  - Ionization source
    - Hard ionization techniques:
      - Electron impact, laser ablation/photoionization
    - Soft ionization techniques:
      - Chemical ionization, electrospray, thermal desorption
  - Mass analyzer
    - Quadrupole: Scans mass range
    - Time-of-flight: Entire mass range at once
    - Tandem MS: Use more than one mass analyzer!
  - Detector
    - Flame ionization
    - Photomultiplier or a multi-channel plate
  - Data analyzer
  - Additional Equipment:
    - Vacuum pumps! Operational Pressure less than $\sim 10^{-5}$ torr
    - High voltage power supplies

Chemical Composition of Particles: GC-MS

- Gas Chromatography-Mass Spectrometry
  - Analysis of gases and dissolved particles
  - Able to resolve complex mixtures of volatile components
  - Precise characterization of **stable** atmospheric species
    - CH_4, N_2O, CFCs and non-sticky organic molecules
    - All data on [CFCs] is obtained via GC-MS
  - Compounds are identified via their retention times and mass spectra
  - Quantitative
  - Little sample required
  - Thermal decomposition

From Skoog, Holler, Nieman

Chemical Composition of Particles: GC-MS

Typical VOC levels from GC-MS

TABLE 11.8 Some Typical Concentration Ranges Measured for Some Small Hydrocarbons from Remote to Urban Areas (ppb)

Compound	Type of air mass		
	Urban	Rural–suburban	Remote
	Brazil,[a] Denmark,[b] India,[c] Japan,[d] Greece,[e] U.K.,[f] U.S.,[i,k,q] Canada,[l,p] Sweden,[m,n] France,[v] Italy,[z] Mexico[y]	Brazil,[a] Denmark,[b] U.S.,[i,k,q] Canada[l,p] Sweden,[m,n] France[v]	U.S.,[i,k,q] Canada,[l,p] France,[v] Antarctic,[p,s] North Atlantic[t]
Ethane	0.6–29	0.4–4	0.4–2
Ethene	0.7–168	0.1–3	0.07–0.4
Acetylene	0.7–44	0.1–3	0.01–0.7
Propane	0.4–221	0.2–2	0.04–0.9
Propene	0.1–39	0.02–2 ·	0.02–0.2
n-Butane	0.02–96	0.1–1	0.1–0.75
Isobutane	0.3–45	0.04–0.6	0.003–0.2
1-Butene	0.2–7	0.01–0.04	0.005–0.014[w]
2-Methyl propene	3–18	0.04–0.16	—
2-Butene (cis and trans)	0.10–4	0.008–0.06	0.006–0.024[w]
n-Pentane	0.7–67	0.07–0.4	0.007–0.19
Isopentane	2–90	0.1–0.6	0.008–0.2
Benzene	0.9–26	0.1–0.6	0.008–0.2
Toluene	2–39	0.05–0.8	0.01–0.25
o-Xylene	0.4–6	0.02–0.2	0.001–0.03
m- and p-Xylene	0.3–30	0.02–0.12	0.002–0.008
1,3-Butadiene	0.1–6	0.03–0.6	0.02–0.13
Isoprene	0.1–2	0.005–5.5	

Finlayson-Pitts

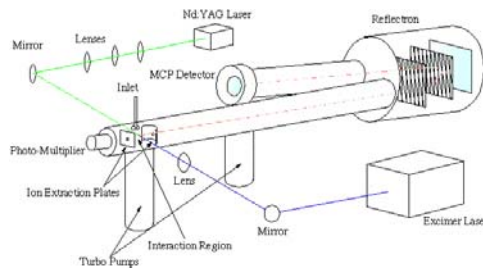# Chemical Composition of Particles

- Real-time single-particle analysis techniques
  - Advantages
    - Much better time resolution than collection methods
    - Can see differences from particle to particle
    - Simultaneous sizing and compositional analysis!
    - Less chance for decompositon, reaction, etc. to occur as a function of time
  - Disadvantages
    - Ionization often involves extensive fragmentation
      - Speciation of organics is difficult
      - Lose molecular weight information
      - Analysis is typically very complex and time consuming
    - Quantitation can be difficult
    - Smallest particles often go undetected

Chemical Composition of Particles: PALMS

- Particle Analysis by Laser Mass Spectrometry
  - Particles enter source region through inlet
  - Pass through the YAG beam and scatter light
    - Acts to size the particle
    - Trips the Excimer laser
  - Excimer ionizes particles
  - Resulting ions are accelerated down a TOF-MS
  - Ion current is measured with a MCP
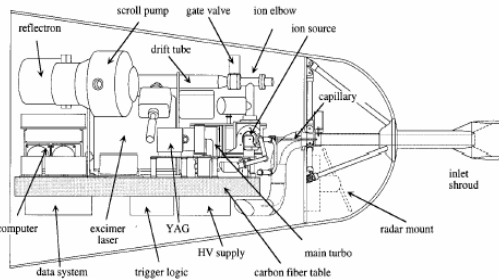
PALMS designed by Dan Murphy at Aeronomy Lab
http://www.al.noaa.gov/PALMS/.

Chemical Composition of Particles: PALMS

FIGURE 3. Schematic layout of the PALMS instrument components. For scale, the carbon fiber table is 122 cm (48˝) long.

- Aircraft deployable
- Remarkable variety in composition of stratospheric and tropospheric aerosols
  - Many contained sulfate and water
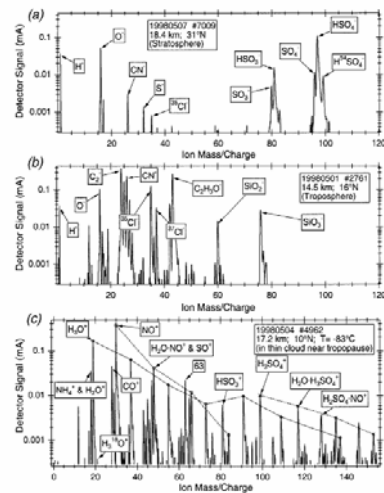 - Many others also contained organics and minerals

Thomson et al. 2000. Aerosol Sci Tech. 33:153-169

FIGURE 6. Sample mass spectra from single aerosol particles at high altitude. (a) A negative ion spectrum of a stratospheric sulfuric acid particle with additional small peaks. (b) A mineral dust and organic particle in the upper troposphere. (c) A positive ion spectrum in a cloud, showing both that the instrument can respond to water, a highly volatile species, and the difficulties caused by water. Ions clustered with water are connected by dotted lines. The NO+ ion does not cluster with large numbers of water molecules.

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Morphology of Particles

- TOF-SIMS
  - Collected particle analysis
  - Soft ionization technique
  - Surface sensitive!
- Surface Spectroscopy
  - Imaging: Distribution of chemical species
  - Static: Chemical composition
  - Dynamic: Depth profiling
- Ionization
  - Pulsed primary ion beam, Ga
  - Desorb and ionize species from the sample surface
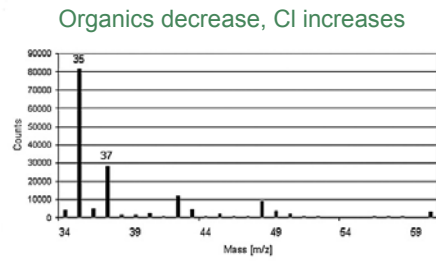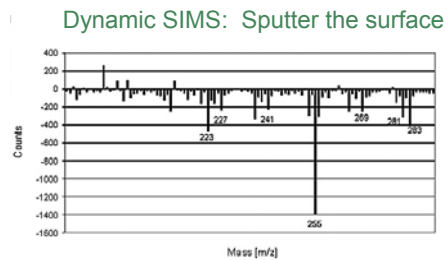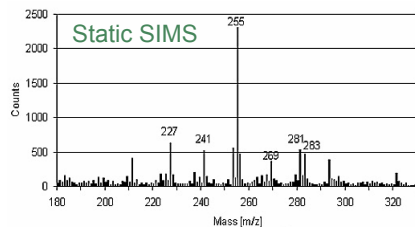 - Secondary ions are detected by TOF-MS

Primary Ion   Secondary Ions

Region of
greatest
damage

Region of
least
damage

From www.phi.com
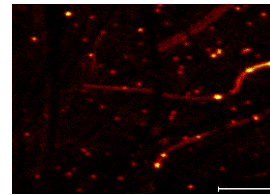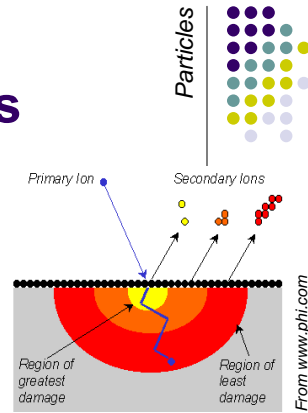
Courtesy of H. Tervahattu

TOF-SIMS image of Cl

Morphology of Particles

- Depth-profiling
  - Fatty acids at the surface
  - Sputter the surface
    - Fatty acids decrease (m/z 255, etc)
    - Increase in Cl (m/z 35, 37)
- Direct evidence of an organic film on a marine aerosols

Dynamic SIMS: Sputter the surface

Counts

227   241   269 281
223   283

255

Mass [m/z]

Organics decrease, Cl increases

Static SIMS

255

227
241   281 283
269

Mass [m/z]

35

37

Mass [m/z]

Figures from Tervahattu et al. 2002. JGR-Atmos. 107(D16), 4319.

Conclusions

- Content of the atmosphere is complex
  - Lots of potential interference
- Concentration of certain species can be very low and vary substantially over time
- Can use many different instruments to analyze similar compounds
  - Each technique has its own set of artifacts
  - Must find ways to compare measurements
- No one instrument can do it all
  - Always looking for complimentary and supplementary information to see the entire picture