

ENVE 576

Indoor Air Pollution

Fall 2017

October 17, 2017

SVOCs and aerosol chemistry
IAQ measurement techniques

Built
Environment
Research
@ IIT



*Advancing energy, environmental, and
sustainability research within the built environment*

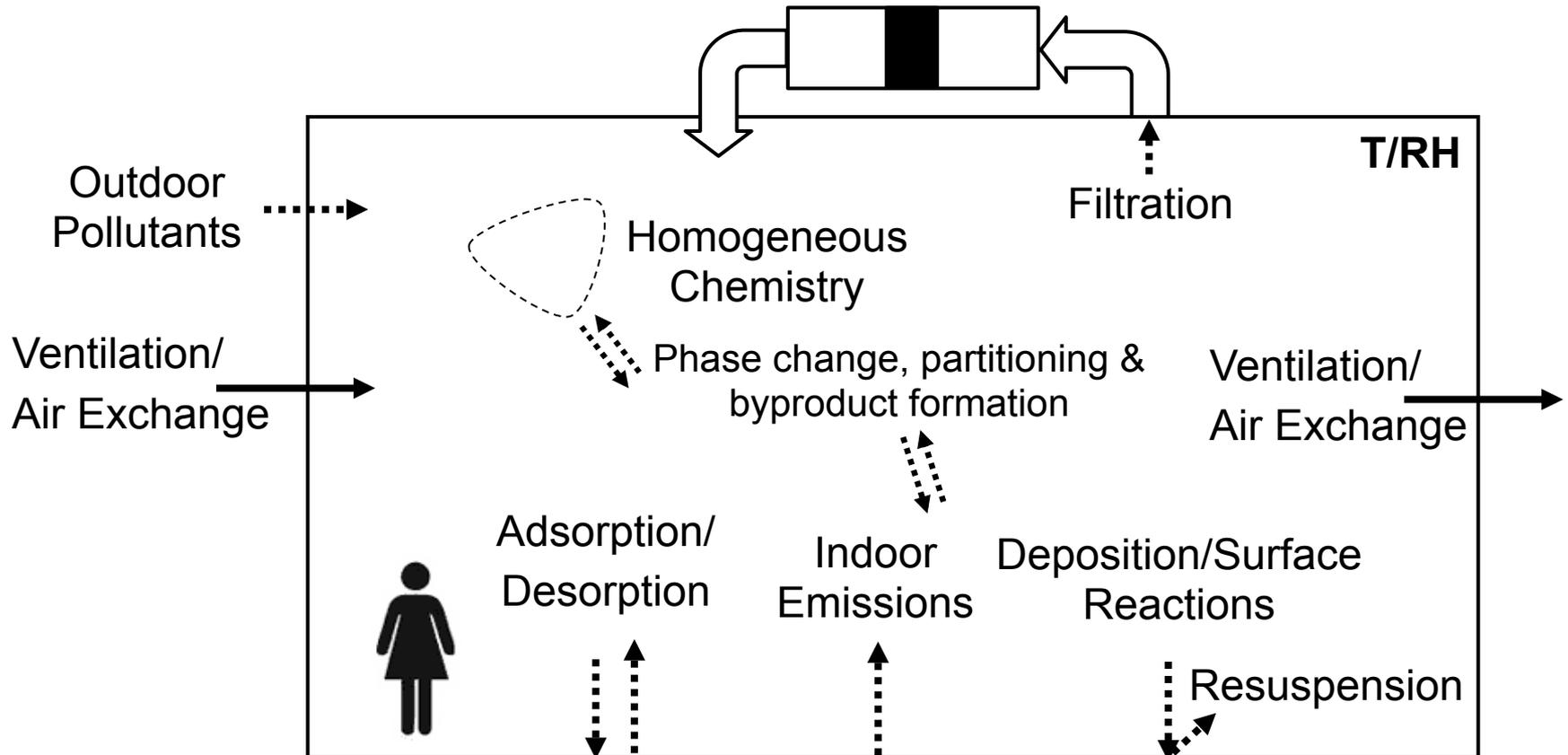
Dr. Brent Stephens, Ph.D.
Department of Civil, Architectural and Environmental Engineering
Illinois Institute of Technology
brent@iit.edu

Built Environment Research Group
www.built-envi.com

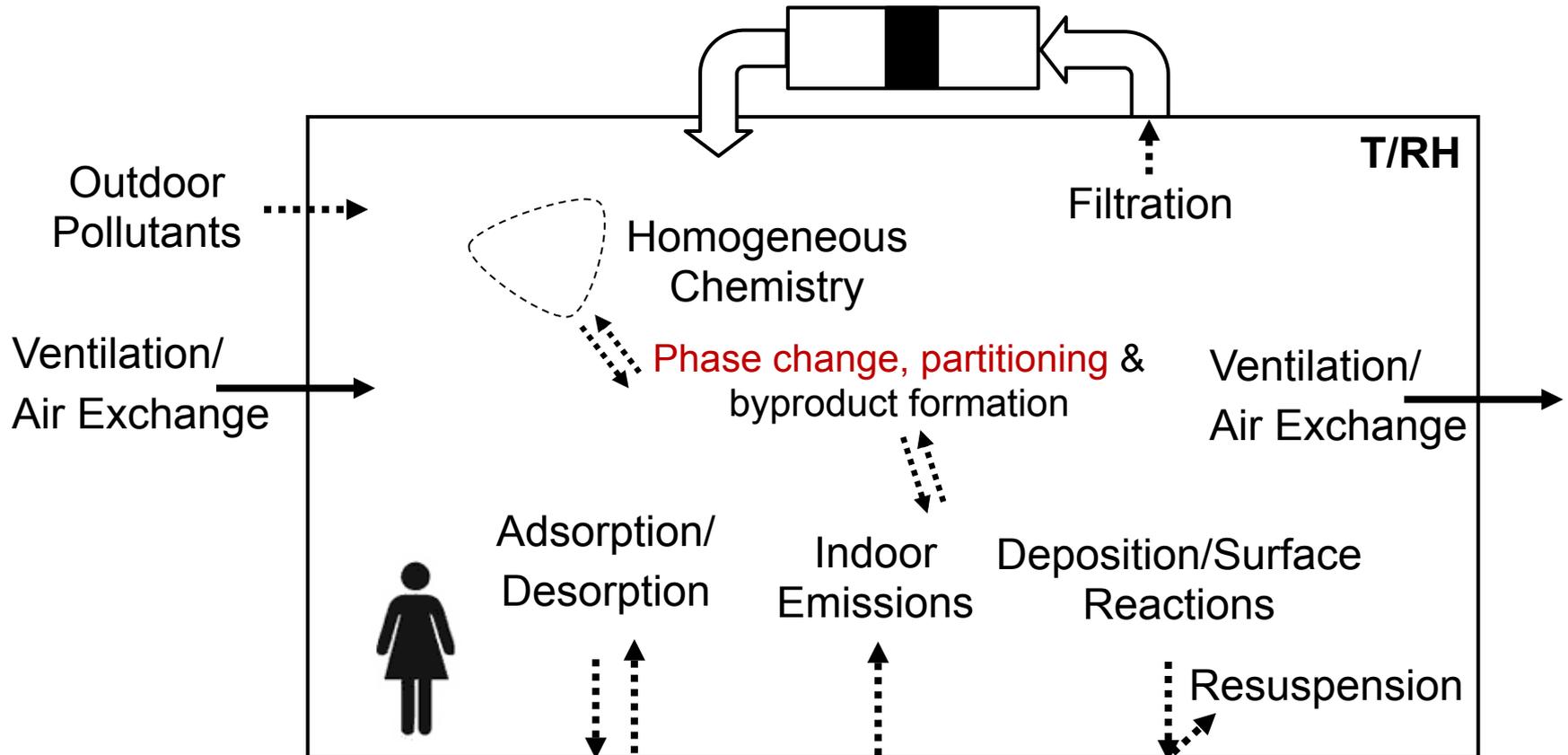
Review from last time

- Last time we covered particle filtration
- HW 4 was assigned, due today
- Next assignments coming up:
 - Blog post #2 due Tuesday October 24
 - Take home exam will be released on October 31, due November 7
 - Final project report due Nov 28
 - With a blog post summarizing your project due as well

Indoor environment: Mass balance



Indoor environment: Mass balance



SEMI-VOLATILE ORGANIC COMPOUNDS

What are semi-volatile organic compounds?

- **Semi-volatile organic compounds (SVOCs)** are organic molecules that can have meaningful abundances in both the gas phase and condensed (particle) phases
 - Sometimes called **particulate organic matter (POM)**
 - Compounds with boiling points from 240 to 400°C
 - Compounds with saturation vapor pressures from 10^{-2} to 10^{-7} kPa

Generally: as $p_{\text{vap,sat}} \uparrow$ BP $\downarrow \rightarrow$ More likely to be in gas phase than solid phase
- SVOCs are generally under-studied relative to VOCs and aerosols
 - Doesn't mean they're not important \rightarrow largely due to analytical limitations
- We've already touched on some of these
 - e.g., polycyclic aromatic hydrocarbons (PAHs) originating from combustion
- SVOCs also occur as active ingredients in pesticides, cleaning agents, and personal care products
 - And as major additives in materials such as floor coverings, furnishings, and electronics components

What are semi-volatile organic compounds?

- Most SVOCs have a slow rate of release from sources
- Exposures can occur via inhalation
 - Both gases and SVOCs adsorbed onto particles
- Exposures can also occur via dermal and ingestion pathways
- Some are known to be toxic
 - Dioxins, benzo[a]pyrene, pentachlorophenol
 - Many have been removed from production over the years
- Others have emerging indicators of concern
 - More than 100 SVOCs have been found in the US population's blood in large biomonitoring studies

Some SVOCs of emerging concern

- Phthalate esters (BBzP, DEHP) (often used as plasticizers)
 - Allergic symptoms in children
 - Slowed male reproductive development
 - Altered semen quality
- Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA)
 - Was a key ingredient in Scotchgard
 - Low birth weight, chronic kidney disease
- Polychlorinated biphenyl (PCBs), brominated flame retardants (BFRs), di-2-ethylhexyl phthalate (DEHP), bisphenol A, and some pesticides
 - Have been linked to **endocrine disrupting (ED) activity**
 - SVOCs that have chemical structures similar to those of human hormones and can either mimic or block endocrine (hormonal) activity
 - EDs may be important contributors to neurodevelopment and behavioral problems ranging from autism to attention deficit disorder
 - Incomplete and sometimes controversial evidence

SVOC classifications, sources, and potential health effects

SVOC Compounds	Uses	Sources	Potential Health Effects
Alkylphenols <i>Example:</i> 4-nonylphenol, 4-octylphenol	Nonionic Surfactants	Detergents, Disinfectants, Surface Cleaners	May Interfere With, Mimic or Block Hormones
Organochlorines <i>Example:</i> DDT, Chlordane	Pesticides, Termiticide, Bactericide (Some Have Been Banned or Restricted in the 1980s)	Outdoor and Indoor Air, Tracked-In Dust, Disinfecting Products	Neurotoxicity, Effects on Developing Reproductive Systems And on Lactation, Cancer
Organophosphorus Compounds <i>Example:</i> Tris(2-chloroethyl)phosphate (TCEP), Tris(chloropropyl)phosphate (TCPP)	Plasticizers, Antifoaming Agents, Flame Retardants, Pesticides	Polymeric Materials, Fabrics, Polyurethane Foams, Electronics (Cable Sheathing and Casings), Outdoor and Indoor Air, Dust	Effects on Neurodevelopment and Growth in Developing Tissue, Relate To Respiratory Disease in Children Through Dysregulation of the Autonomic Nervous System
Phthalates <i>Example:</i> Di(2-ethylhexyl)-phthalate (DEHP), Di-iso-nonyl-phthalate (DINP)	Plasticizers, Solvents, Fixing Fragrances (Use of DEHP And BBP Reduced Due to the Concern on Health Effects)	Flexible PVC, PVC Flooring, Wall Covering, Electrical Cable and Casings, Personal Care Products	Effects on the Development of Male Reproductive Tract, Prenatal Mortality, Reduced Growth and Birth Weight, May Relate to Asthma and Allergies in Children
Polybrominated Diphenyl Ethers (PBDEs) <i>Example:</i> Hexabromodiphenyl ether (BDE-153), Tetrabromodiphenyl ether (BDE-47)	Flame Retardants (Use of Penta- and Octa-BDEs Have Been Restricted)	Carpet Padding, Wall Coverings, Electronics (Casings), Furniture (Foam Cushioning and Mattress)	Effects on the Development of Brain And Nerve Tissues, Permanent Learning and Memory Impairment, Behavioral Changes, Delayed Puberty Onset, Fetal Malformations, Thyroid Hormone Disruption

SVOC classifications, sources, and potential health effects

SVOC Compounds	Uses	Sources	Potential Health Effects
Polychlorinated Biphenyls (PCBs) <i>Example:</i> 2,2',5,5'-tetrachloro-1,1'-biphenyl (PCB 52), 2,2',4,4',5,5'-hexachloro-1,1'-biphenyl (PCB 153)	Heat Transfer Fluids, Stabilizers, Flame Retardants, (Have Been Banned or Restricted in the 1970s)	Floor Finishes, Foam Cushioning and Mattresses, Oil-Filled Transformers, Capacitors	Developmental Neurotoxicants, Effects on Immune, Reproductive, Nervous, and Endocrine Systems, Cancer (Including Breast Cancer)
Polycyclic Aromatic Hydrocarbons (PAHs) <i>Example:</i> Benzo(a)pyrene, Pyrene	Combustion Byproducts	Outdoor Air, Cooking, Smoking	Cataracts, Kidney and Liver Damage, Jaundice, Increased Risk Of Skin, Lung, Bladder, and Gastrointestinal Cancers
Pyrethroids <i>Example:</i> Cyfluthrin, Permethrin	Insecticides	Outdoor and Indoor Air, Tracked-In Dust, Cleaning Products	Weak Anti-Androgenic, Anti-Estrogenic, or Estrogenic Effect
Parabens <i>Example:</i> Butyl paraben, Methyl paraben	Bactericides, Antimicrobial Agents, Preservatives	Personal Care Products, Canned Food, Fabrics	Weak Environmental Estrogens

Semi-volatile organic compounds found indoors

Table 1
Selected semivolatile organic compounds observed or expected in indoor environments, organized by product class and chemical class, with examples.

Chemical class	Specific chemical	CAS No.	Formula	log P_5^a
<i>Biocides and preservatives</i>				
Antimicrobials	Triclosan	3380-34-5	C ₁₂ H ₇ Cl ₃ O ₂	-8.9
Antioxidants	Butylated hydroxytoluene (BHT)	128-37-0	C ₁₅ H ₂₄ O	-6.7
Fungicides	Tributyltin oxide (TBTO)	56-35-9	C ₂₄ H ₅₄ OSn ₂	-10.9
Wood preservatives	Pentachlorophenol (PCP)	87-86-5	C ₆ HCl ₅ O	-7.4
<i>Combustion byproducts</i>				
Environmental tobacco smoke	Nicotine	54-11-5	C ₁₀ H ₁₄ N ₂	-4.7
Polychlorinated dibenzo- <i>p</i> -dioxins	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin (TCDD)	1746-01-6	C ₁₂ H ₄ Cl ₄ O ₂	-11.4
Polycyclic aromatic hydrocarbons	Benzo[<i>a</i>]pyrene (BaP)	50-32-8	C ₂₀ H ₁₂	-10.5
Polycyclic aromatic hydrocarbons	Phenanthrene	85-01-8	C ₁₄ H ₁₀	-6.6
Polycyclic aromatic hydrocarbons	Pyrene	129-00-0	C ₁₆ H ₁₀	-7.5
<i>Degradation products/residual monomers</i>				
Phenols	Bisphenol A	80-05-7	C ₁₅ H ₁₆ O ₂	-10.5
<i>Flame retardants</i>				
Brominated flame retardants	2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	68631-49-2	C ₁₂ H ₄ Br ₆ O	-13.8
Brominated flame retardants	2,2',4,4',5-Pentabromodiphenyl ether (BDE-99)	60348-60-9	C ₁₂ H ₅ Br ₅ O	-12.0
Brominated flame retardants	2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	5436-43-1	C ₁₂ H ₆ Br ₄ O	-10.5
Chlorinated flame retardants	Perchloropentacyclodecane (mirex)	2385-85-5	C ₁₀ Cl ₁₂	-10.6
Phosphate esters	Tris(chloropropyl) phosphate	13674-84-5	C ₉ H ₁₈ Cl ₃ O ₄ P	-6.3
<i>Heat-transfer fluids</i>				
Polychlorinated biphenyls (PCBs)	2,2',5,5'-tetrachloro-1,1'-biphenyl (PCB 52)	35693-99-3	C ₁₂ H ₆ Cl ₄	-7.8
Polychlorinated biphenyls (PCBs)	2,2',4,4',5,5'-hexachloro-1,1'-biphenyl (PCB 153)	35065-27-1	C ₁₂ H ₄ Cl ₆	-9.8
<i>Microbial emissions</i>				
Sesquiterpenes	Geosmin	23333-91-7	C ₁₂ H ₂₂ O	-5.3
<i>Personal care products</i>				
Musk compounds	Galaxolide	1222-05-5	C ₁₈ H ₂₆ O	-7.5
Petrolatum constituents	<i>n</i> -Pentacosane	629-99-2	C ₂₅ H ₅₂	-10.2

Semi-volatile organic compounds found indoors

Table 1

Selected semivolatile organic compounds observed or expected in indoor environments, organized by product class and chemical class, with examples.

Chemical class	Specific chemical	CAS No.	Formula	log P_5^a
<i>Pesticides/termiticides/herbicides</i>				
Carbamates	Propoxur	114-26-1	C ₁₁ H ₁₅ NO ₃	-6.8
Organochlorine pesticides	Chlordane	57-74-9	C ₁₀ H ₆ Cl ₈	-7.8
Organochlorine pesticides	<i>p,p'</i> -DDT	50-29-3	C ₁₄ H ₉ Cl ₅	-9.7
Organophosphate pesticides	Chlorpyrifos	2921-88-2	C ₉ H ₁₁ Cl ₃ NO ₃ PS	-7.9
Organophosphate pesticides	Diazinon	333-41-5	C ₁₂ H ₂₁ N ₂ O ₃ PS	-8.0
Organophosphate pesticides	Methyl parathion	298-00-0	C ₈ H ₁₀ NO ₅ PS	-6.6
Pyrethroids	Cyfluthrin	68359-37-5	C ₂₂ H ₁₈ Cl ₂ FNO ₃	-12.4
Pyrethroids	Cypermethrin	52315-07-8	C ₂₂ H ₁₉ Cl ₂ NO ₃	-12.4
Pyrethroids	Permethrin	52645-53-1	C ₂₁ H ₂₀ Cl ₂ O ₃	-10.7
Synergist	Piperonyl butoxide	51-03-6	C ₁₉ H ₃₀ O ₅	-10.1
<i>Plasticizers</i>				
Adipate esters	Di(2-ethylhexyl) adipate (DEHA)	103-23-1	C ₂₂ H ₄₂ O ₄	-9.9
Phosphate esters	Triphenylphosphate (TPP)	115-86-6	C ₁₈ H ₁₅ O ₄ P	-9.2
Phthalate esters	Butylbenzyl phthalate (BBzP)	85-68-7	C ₁₉ H ₂₀ O ₄	-10.0
Phthalate esters	Dibutyl phthalate (DBP)	84-74-2	C ₁₆ H ₂₂ O ₄	-8.0
Phthalate esters	Di(2-ethylhexyl) phthalate (DEHP)	117-81-7	C ₂₄ H ₃₈ O ₄	-11.5
<i>Sealants</i>				
Silicones	Tetradecamethylcycloheptasiloxane (D7)	107-50-6	C ₁₄ H ₄₂ O ₇ Si ₇	-
<i>Stain repellents, oil and water repellents</i>				
Perfluorinated surfactants	<i>N</i> -ethyl perfluorooctane sulfonamidoethanol (EtFOSE)	1691-99-2	C ₁₂ H ₁₀ F ₁₇ NO ₃ S	-6.8
Perfluorinated surfactants	<i>N</i> -methylperfluorooctane sulfonamidoethanol (MeFOSE)	24448-09-7	C ₁₁ H ₈ F ₁₇ NO ₃ S	-6.4
<i>Surfactants (nonionic), emulsifiers, coalescing agents</i>				
Alkylphenol ethoxylates	4-Nonylphenol	104-40-5	C ₁₅ H ₂₄ O	-7.1
Coalescing agents	3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate (Texanol)	25625-77-4	C ₁₂ H ₂₄ O ₃	-5.6
<i>Terpene oxidation products</i>				
	Pinonaldehyde	2704-78-1	C ₁₀ H ₁₆ O ₂	-4.1
<i>Water disinfection products</i>				
	3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX)	77439-76-0	C ₅ H ₃ Cl ₃ O ₃	-9.3
<i>Waxes, polishes and essential oils</i>				
Fatty acids	Stearic acid (octadecanoic acid)	57-11-4	C ₁₈ H ₃₆ O ₂	-11.0
Fatty acids	Linoleic acid	60-33-3	C ₁₈ H ₃₂ O ₂	-10.2
Sesquiterpenes	Caryophyllene	87-44-5	C ₁₅ H ₂₄	-4.6

SVOC 'partitioning'

SVOCs can exist in both gas and particle phases

$$\phi = \frac{\text{particle phase concentration}}{\text{total gas + particle phase concentration}} = \frac{k * SA_{\text{particles}}}{p_{\text{vap,sat}} + k * SA_{\text{particles}}}$$

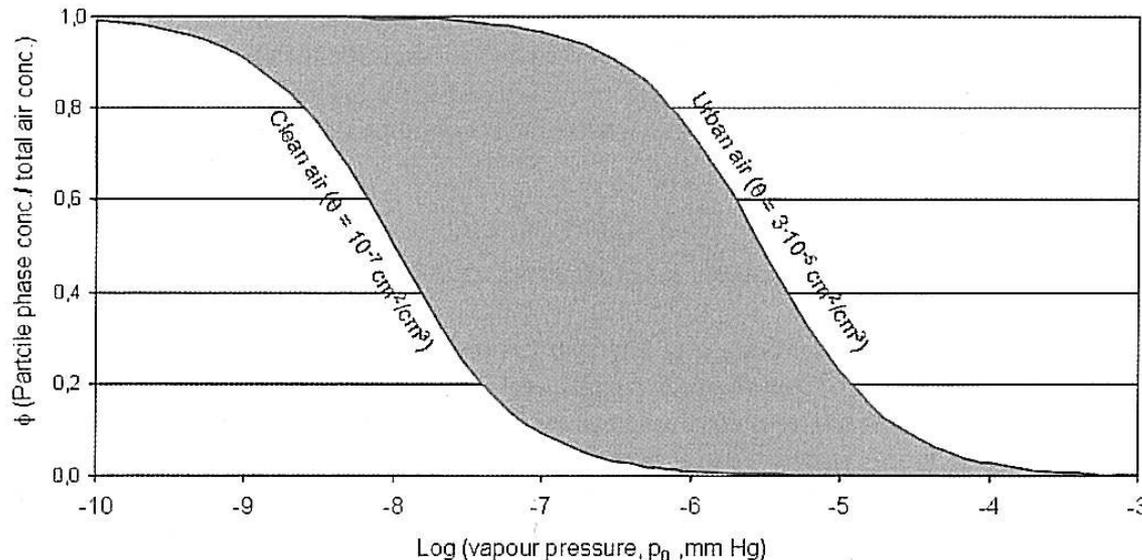
ϕ = concentration of a compound in the particle phase relative to the total air concentration (gas + particle) [dimensionless]

k = constant that depends on MW of compound

$SA_{\text{particles}}$ = aerosol surface area per volume [cm^2/cm^3]

$p_{\text{vap,sat}}$ = saturation vapor pressure of compound (mm Hg)

Generally: as VP \uparrow BP \downarrow \rightarrow More likely to be in gas phase than solid phase



And: the more PM there is to adsorb/partition on to, the more you'll have in the particle phase

Organic gases: VOCs

- VOCs, VVOCs, SVOCs, and POM are all categorized by their boiling points
 - Lower molecular weight (and low boiling point) compounds are more likely in the gas-phase

Table 1. Classification of indoor organic pollutants

Category	Description	Abbreviation	Boiling-point range (°C) ^a	Sampling methods typically used in field studies
1	Very volatile (gaseous) organic compounds	VVOC	<0 to 50-100	Batch sampling; adsorption on charcoal
2	Volatile organic compounds	VOC	50-100 to 240-260	Adsorption on Tenax, carbon molecular black or charcoal
3	Semivolatile organic compounds	SVOC	240-260 to 380-400	Adsorption on polyurethane foam or XAD-2
4	Organic compounds associated with particulate matter or particulate organic matter	POM	>380	Collection on filters.

^a Polar compounds appear at the higher end of the range.

SVOC 'partitioning'

We can also describe particle/gas partitioning as a function of the total aerosol mass concentration suspended in the air (TSP):

$$K_p = \frac{(F / TSP)}{c_g} = \frac{c_p}{c_g}$$

K_p = thermodynamic particle-gas partition coefficient [$\text{m}^3/\mu\text{g}$]

F = equilibrium particle phase concentration of a compound [ng/m^3]

TSP = concentration of total suspended particles [$\mu\text{g}/\text{m}^3$]

c_g = equilibrium gas phase concentration (ng/m^3)

c_p = concentration within the particle phase (ng/m^3)

$$\frac{F}{c_g} = K_p(TSP)$$

How do we get K_p ?

Remember: as VP \uparrow BP \downarrow \rightarrow More likely to be in gas phase than solid phase

SVOC 'partitioning'

- Ratio between organic compound's particle phase concentration and its gas phase concentration:

$$\frac{F}{C_g} = K_p(TSP)$$

K_p = thermodynamic particle-gas partition coefficient [$\text{m}^3/\mu\text{g}$]
 F = equilibrium particle concentration of a compound [ng/m^3]
 TSP = concentration of total suspended particles [$\mu\text{g}/\text{m}^3$]
 C_g = equilibrium gas phase concentration (ng/m^3)

$\log(K_p)$ is higher for lower $\log(p_{vap,sat})$

K_p is therefore higher for lower $p_{vap,sat}$

Higher K_p means greater fraction F in the particle phase

Lower vapor pressure more likely to be in solid phase... makes sense, right?

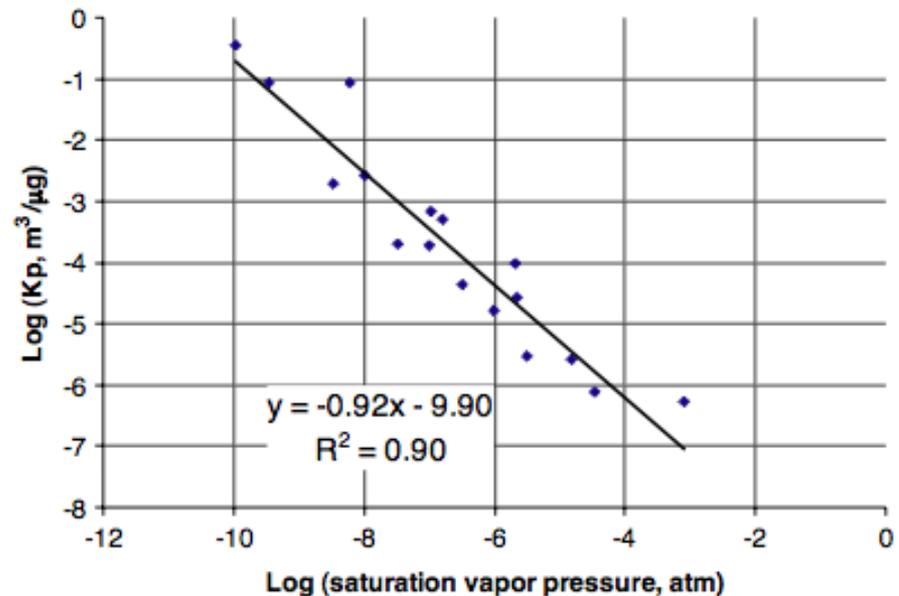


Fig. 1. $\log(K_p)$ versus \log (saturation vapor pressure at 31°C) for a series on n -alkanes and PAHs sorbed to particles generated from gasoline vapors. Data taken from Liang et al. (1997).

SVOC 'partitioning'

- Rule of thumb: higher MW compounds will have lower vapor pressures and thus be more likely to be in the particle phase (higher K_p , F , and c_p)

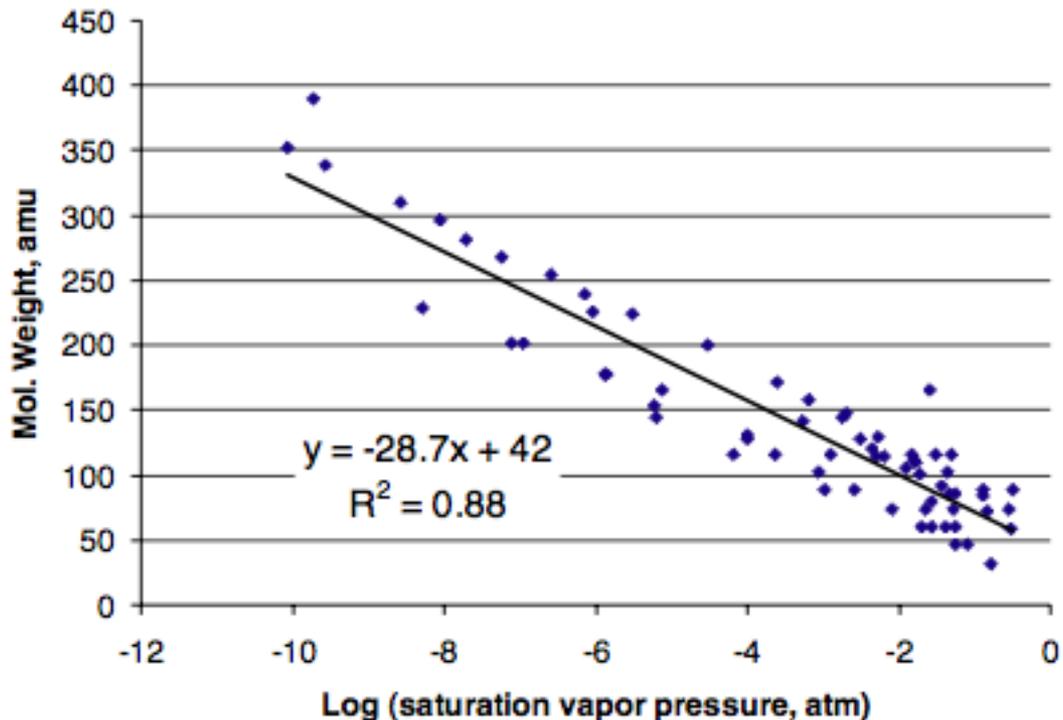


Fig. 6. Log (molecular weight, amu) versus log (saturation vapor pressure at 25°C) for compounds plotted in Figs. 1–3 and 5, as well as DEHP.

SVOCs in indoor environments

Mass balance. SVOCs emitted from indoor materials exist as:

- Gases
- Attached to particles
- Adsorbed to surfaces

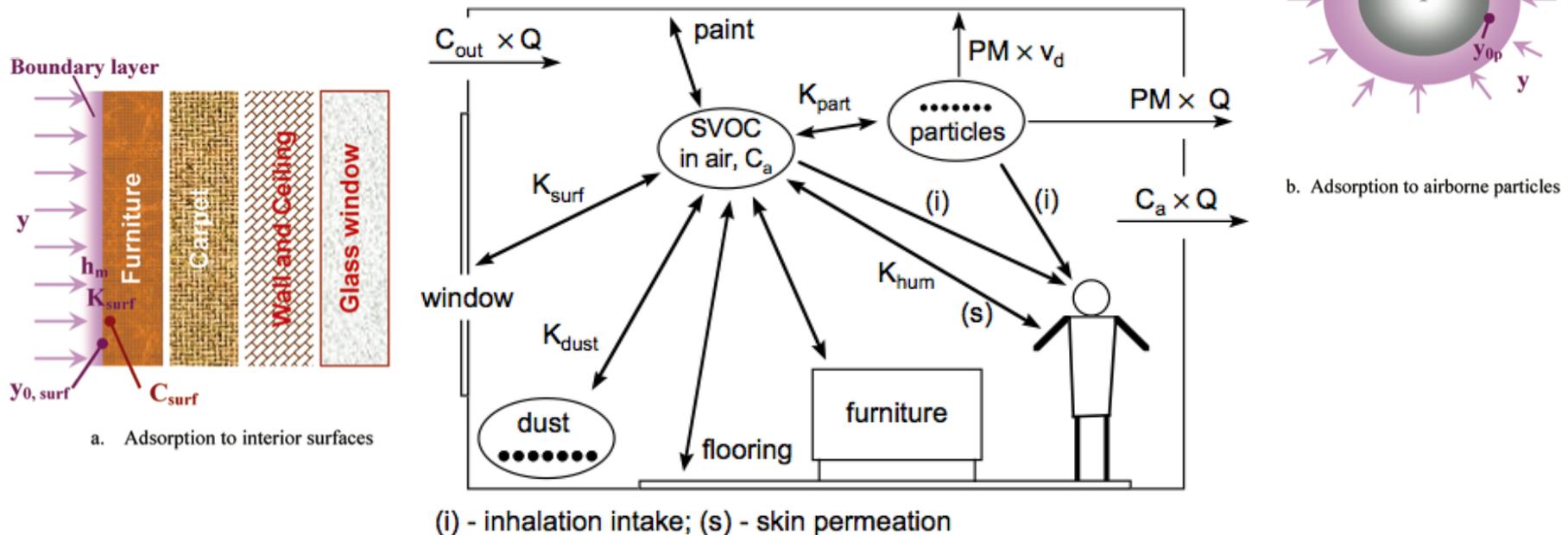


Fig. 3. Schematic illustration of some key aspects of indoor SVOC dynamics. The figure emphasizes the partitioning of an SVOC between the gas phase and different indoor sorptive compartments (airborne particles, settled dust, fixed surfaces, and human surfaces). Also shown are SVOC exchanges with outdoor air associated with ventilation. Important, but not illustrated, are emissions from indoor sources.

Predicted gas, particle, and surface concentrations of different SVOCs

Distribution of selected organic compounds between the gas phase and the surfaces of airborne particles, a carpet and walls within a typical room

Compound	Mol. weight (amu)	Vapor pressure at 25°C (atm)	Assumed gas phase concentration ($\mu\text{g m}^{-3}$)	Mass in gas phase (μg)	Mass on particles (μg)	Mass on carpet (μg)	Mass on walls (μg)
MTBE	88	3.2E-01	10	400	2.3E-5	17	19
Toluene	92	3.7E-02	10	400	1.4E-4	100	70
Ethylbenzene	106	1.3E-02	10	400	3.6E-4	260	140
Propylbenzene	120	4.5E-03	10	400	8.9E-4	610	260
Naphthalene	128	1.0E-04	5	200	1.2E-2	7400	1390
Acenaphthene	154	5.9E-06	5	200	0.13	8.0E+4	8000
Hexadecane	226	9.1E-07	5	200	0.66	3.8E+5	2.6E+4
Phenanthrene	178	1.4E-06	1	40	0.093	5.4E+4	4000
Octadecane	254	2.5E-07	1	40	0.40	2.3E+5	1.1E+4
Pyrene	202	7.6E-08	1	40	1.1	6.2E+5	2.4E+4
Heneicosane	296	8.7E-09	0.5	20	3.6	1.9E+6	4.6E+4
Chrysene	228	5.0E-09	0.5	20	5.8	3.0E+6	6.4E+4
Tetracosane	338	2.8E-10	0.01	0.4	1.4	6.9E+5	7800
DEHP	390	1.9E-10	0.07	3.0	14	6.7E+6	6.9E+4
Pentacosane	352	8.7E-11	0.01	0.4	3.8	1.8E+6	1.6E+4

Values derived for a $3 \times 3.65 \times 3.65 \text{ m}^3$ room containing $20 \mu\text{g m}^{-3}$ of airborne particles (TSP), a 10 m^2 carpet with pad, and painted gypsum board walls. See text for further details.

What are typical indoor SVOC concentrations?

Indoor concentrations and body burden of selected semivolatile organic compounds.

Chemical	Typical reported concentrations in indoor environments				US body burdens (95%ile) ^a – blood (ng g ⁻¹ serum); urine (µg g ⁻¹ creatinine)
	Air (ng m ⁻³)	References	Dust (µg g ⁻¹)	References	
<i>Biocides and preservatives</i>					
Triclosan	–	–	0.2–2	Canosa et al., 2007	360 (urine) ^b
Tributyltin oxide (TBTO)	–	–	0.01–0.1	Fromme et al., 2005	–
Pentachlorophenol (PCP)	0.4–4	Rudel et al., 2003; Morgan et al., 2004	0.2–2	Rudel et al., 2003	2.3 (urine)
<i>Combustion byproducts</i>					
Nicotine	200–2000	Leaderer and Hammond, 1991; Gehring et al., 2006	10–100	Hein et al., 1991; Matt et al., 2004	2.2 (blood) ^c
Benzo[a]pyrene (BaP)	0.02–0.2	Naumova et al., 2002; Morgan et al., 2004	0.2–2	Rudel et al., 2003; Mannino and Orecchio, 2008	0.18 (urine)
Phenanthrene	10–100	Naumova et al., 2002	0.2–2	Mannino and Orecchio, 2008	1.7 (urine) ^d
Pyrene	1–10	Naumova et al., 2002; Rudel et al., 2003	0.2–2	Mannino and Orecchio, 2008	0.24 (urine)
<i>Degradation products/residual monomers</i>					
Bisphenol A	0.5–5	Morgan et al., 2004	0.2–2	Rudel et al., 2003	11 (urine) ^e
<i>Flame retardants</i>					
2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153, hexa BDE)	0.002–0.02	Wilford et al., 2004; Shoeb et al., 2004; Allen et al., 2007	0.03–0.3	Stapleton et al., 2005; Wilford et al., 2005; Wu et al., 2007	0.44 (blood) ^f
2,2',4,4',5-Pentabromodiphenyl ether (BDE-99, pentaBDE)	0.03–0.3	Wilford et al., 2004; Shoeb et al., 2004; Allen et al., 2007	0.4–4	Rudel et al., 2003; Stapleton et al., 2005; Wilford et al., 2005; Wu et al., 2007	0.28 (blood) ^f
2,2',4,4'-Tetrabromodiphenyl ether (BDE-47, tetra BDE)	0.06–0.6	Wilford et al., 2004; Shoeb et al., 2004; Allen et al., 2007	0.3–3	Stapleton et al., 2005; Wilford et al., 2005; Wu et al., 2007	1.1 (blood) ^f
Perchloropentacyclodecane (Mirex)	–	–	–	–	0.41 (blood)
Tris(chloropropyl) phosphate	6–60	Wensing et al., 2005	0.3–3	Wensing et al., 2005	–

What are typical indoor SVOC concentrations?

Indoor concentrations and body burden of selected semivolatile organic compounds.

Chemical	Typical reported concentrations in indoor environments				US body burdens (95%ile) ^a – blood (ng g ⁻¹ serum); urine (µg g ⁻¹ creatinine)
	Air (ng m ⁻³)	References	Dust (µg g ⁻¹)	References	
<i>Personal care products</i>					
Galaxolide	25–250	Fromme et al., 2004	0.5–5	Fromme et al., 2004	–
<i>Pesticides/termiticides/herbicides</i>					
Propoxur	0.8–8	Rudel et al., 2003	0.05–0.5	Rudel et al., 2003	<1 (urine)
Chlordane	0.5–5	Morgan et al., 2004; Offenberg et al., 2004	0.04–0.4	Rudel et al., 2003	0.35 (blood)
<i>p,p'</i> -DDT	0.2–2	Rudel et al., 2003	0.1–1	Rudel et al., 2003	0.18 (blood)
Chlorpyrifos	1–10	Morgan et al., 2004	0.08–0.8	Julien et al., 2008; Morgan et al., 2004	9.2 (urine)
Diazinon	1–5	Morgan et al., 2004	0.02–0.2	Julien et al., 2008	<1 (urine)
Methyl parathion	0.05–0.5	Rudel et al., 2003	0.01–0.1	Rudel et al., 2003	2.9 (urine)
Cyfluthrin	0.1–1.0	Morgan et al., 2004	0.08–0.8	Julien et al., 2008; Morgan et al., 2004	Common metabolite: 2.6 (urine)
Cypermethrin	–	–	0.08–0.8	Julien et al., 2008; Rudel et al., 2003	
Permethrin	0.1–0.7	Rudel et al., 2003; Morgan et al., 2004	0.2–2	Rudel et al., 2003; Julien et al., 2008	3.8 (urine)
Piperonyl butoxide	0.1–1.0	Rudel et al., 2003	0.1–1.0	Rudel et al., 2003	–
<i>Plasticizers</i>					
Di(2-ethylhexyl) adipate (DEHA)	5–15	Rudel et al., 2003	2–10	Rudel et al., 2003	–
Triphenylphosphate (TPP)	0.1–1	Wensing et al., 2005	2–20	Wensing et al., 2005	–

Indoor SVOC behavior w/ different sample areas

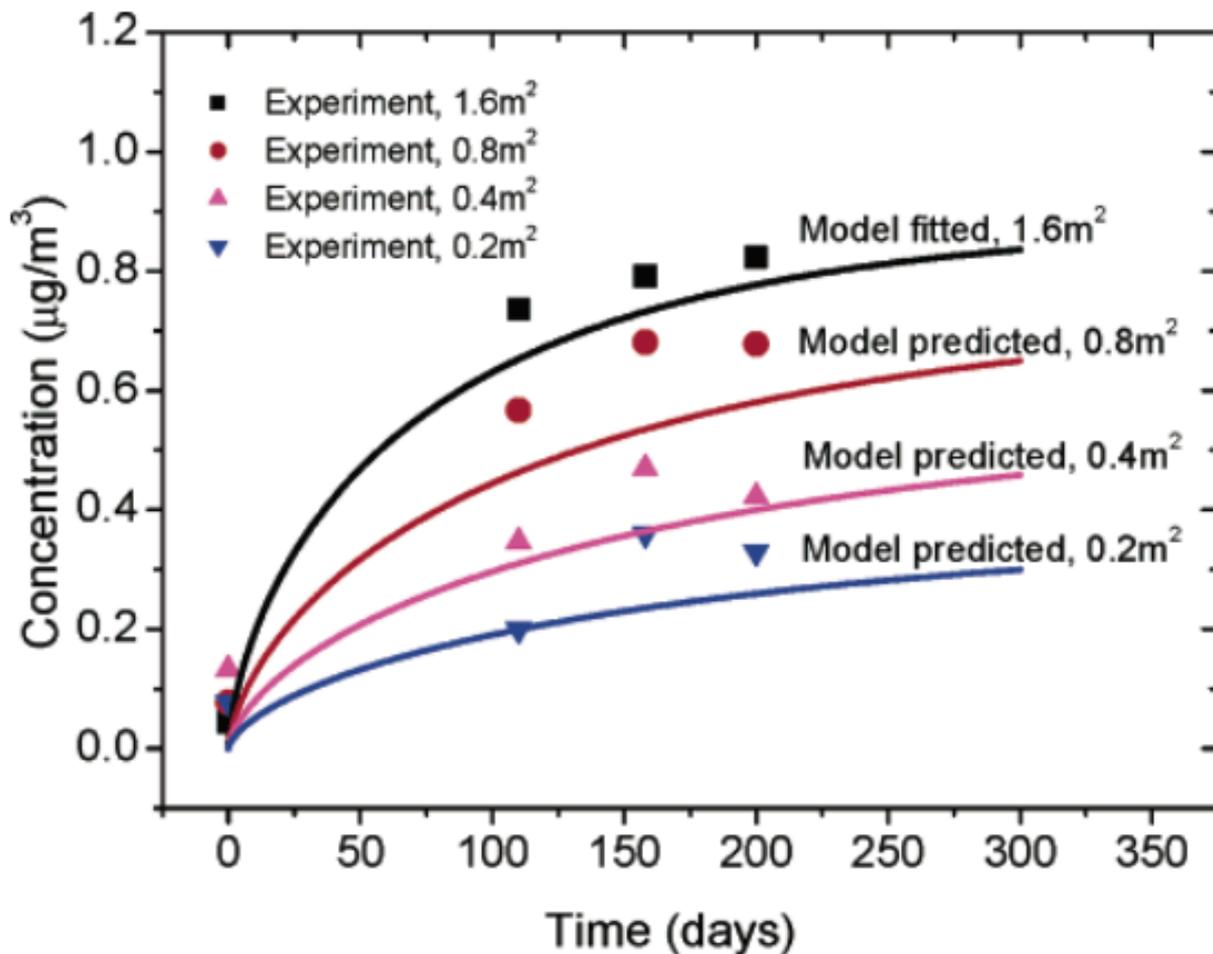


FIGURE 2. Comparison of fitted and predicted gas-phase DEHP concentrations with data measured in CLIMPAQ.

Indoor SVOC behavior w/ material/air partitioning

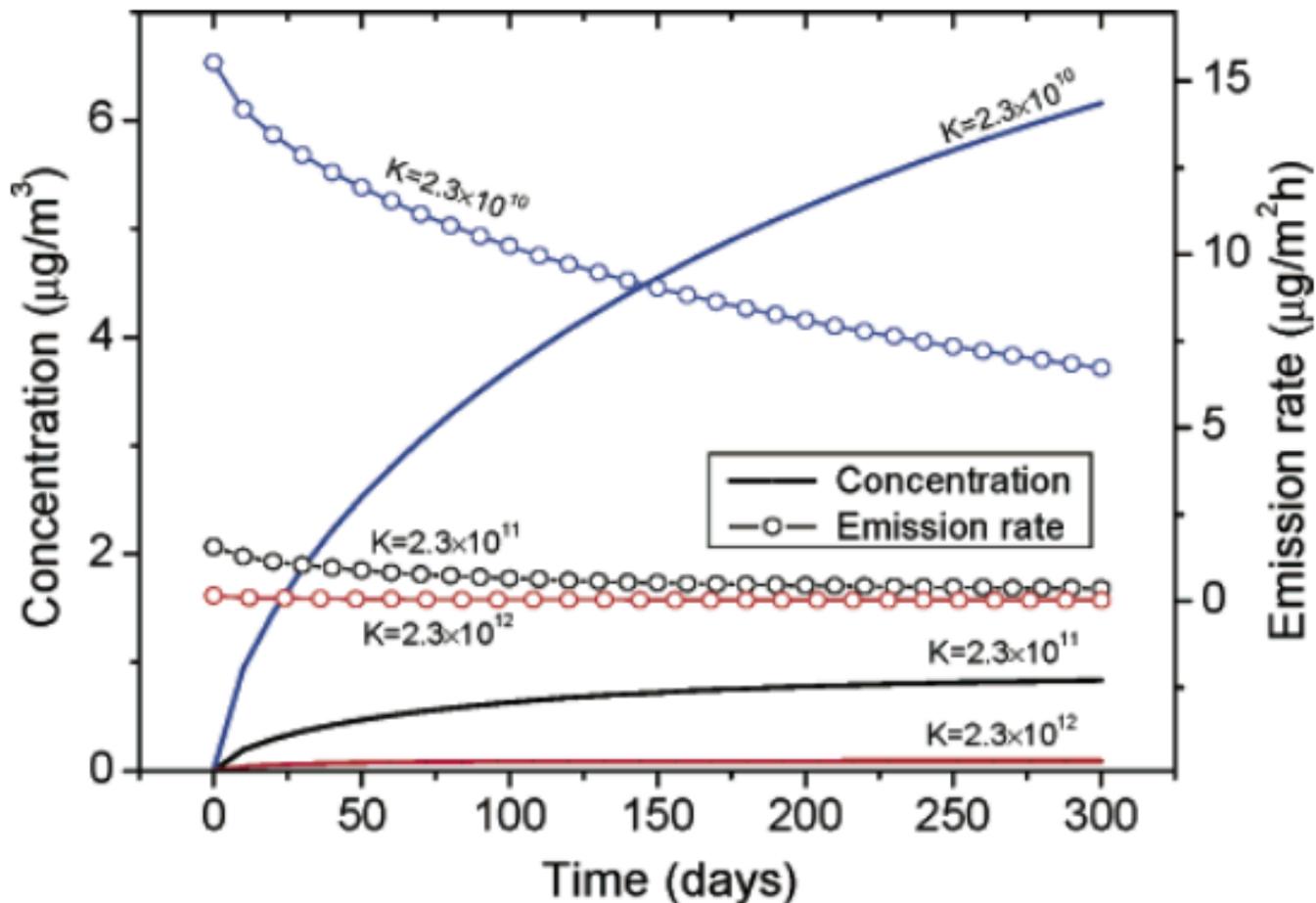


FIGURE 5. Influence of the material/air partition coefficient (K) on SVOC emission rate and gas-phase concentration.

Indoor SVOC behavior w/ surface area

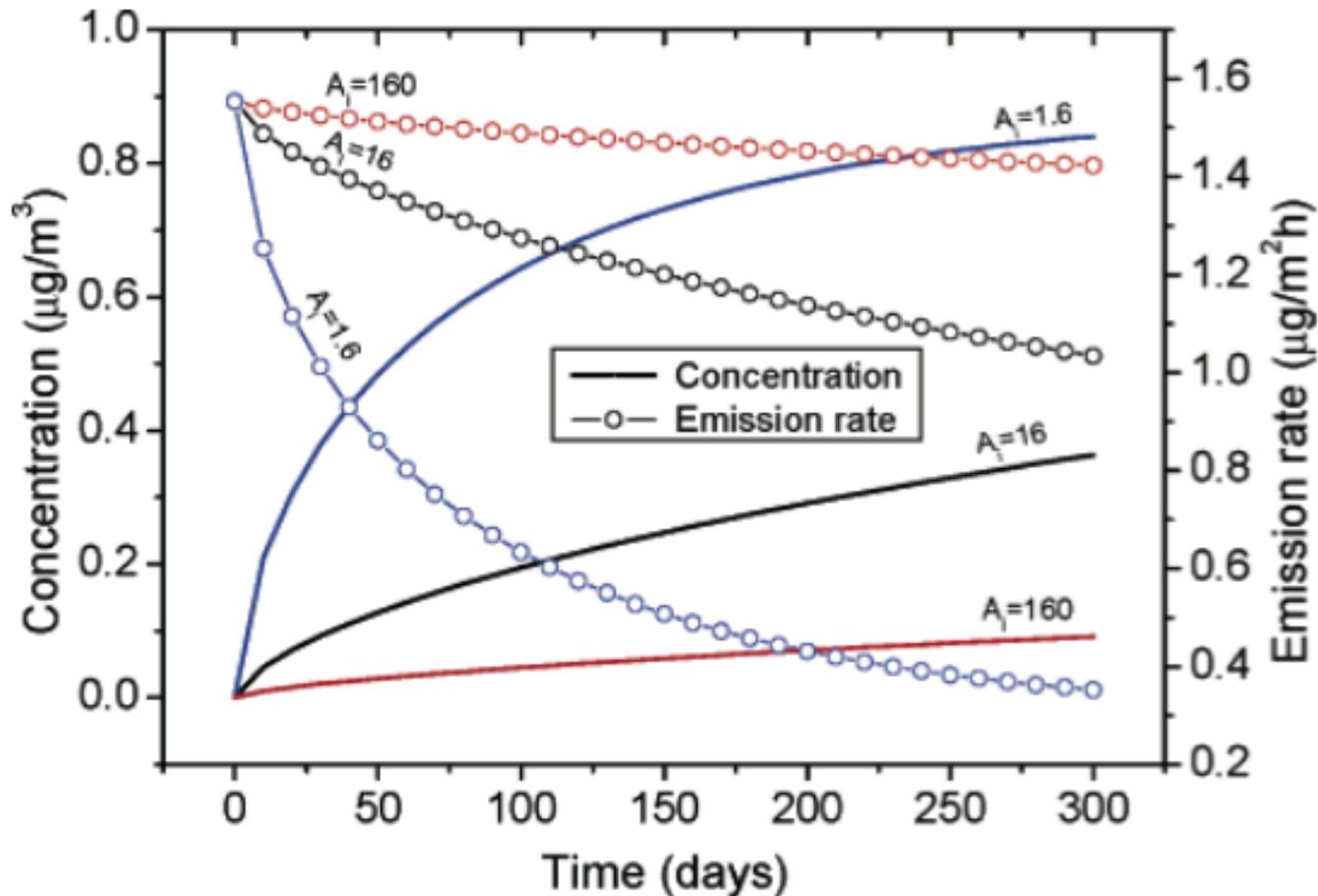


FIGURE 7. Influence of internal surface area (A_i) on SVOC emission rate and gas-phase concentration.

Indoor SVOC behavior w/ suspended particles

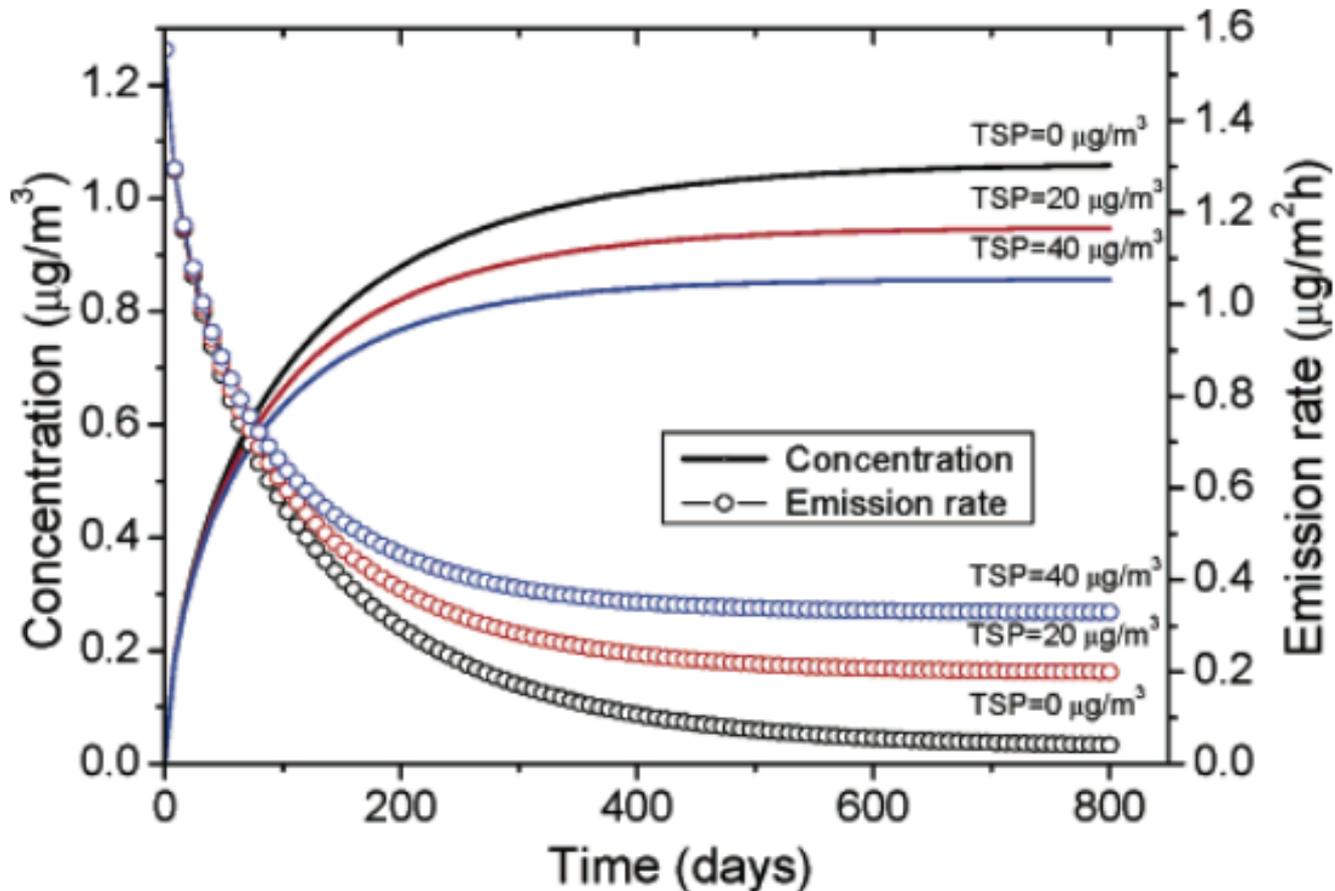


FIGURE 9. Influence of total suspended particle concentration on DEHP emission rate and gas-phase DEHP concentration.

Transdermal uptake of DEHP and DnBP

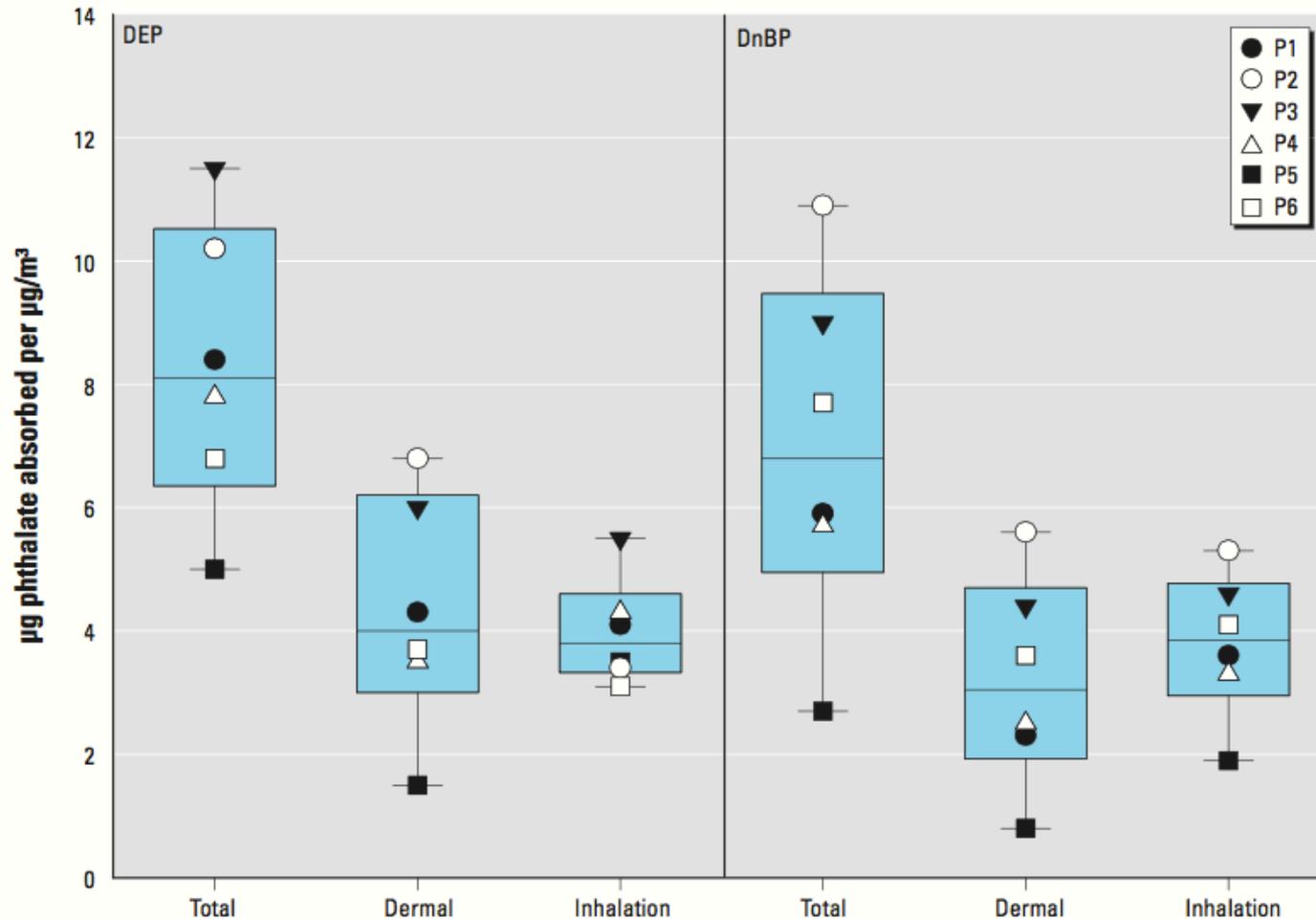
Transdermal Uptake of Diethyl Phthalate and Di(*n*-butyl) Phthalate Directly from Air: Experimental Verification

OBJECTIVES: This study investigated transdermal uptake, directly from air, of diethyl phthalate (DEP) and di(*n*-butyl) phthalate (DnBP) in humans.

METHODS: In a series of experiments, six human participants were exposed for 6 hr in a chamber containing deliberately elevated air concentrations of DEP and DnBP. The participants either wore a hood and breathed air with phthalate concentrations substantially below those in the chamber or did not wear a hood and breathed chamber air. All urinations were collected from initiation of exposure until 54 hr later. Metabolites of DEP and DnBP were measured in these samples and extrapolated to parent phthalate intakes, corrected for background and hood air exposures.

Transdermal uptake of DEP and DnBP

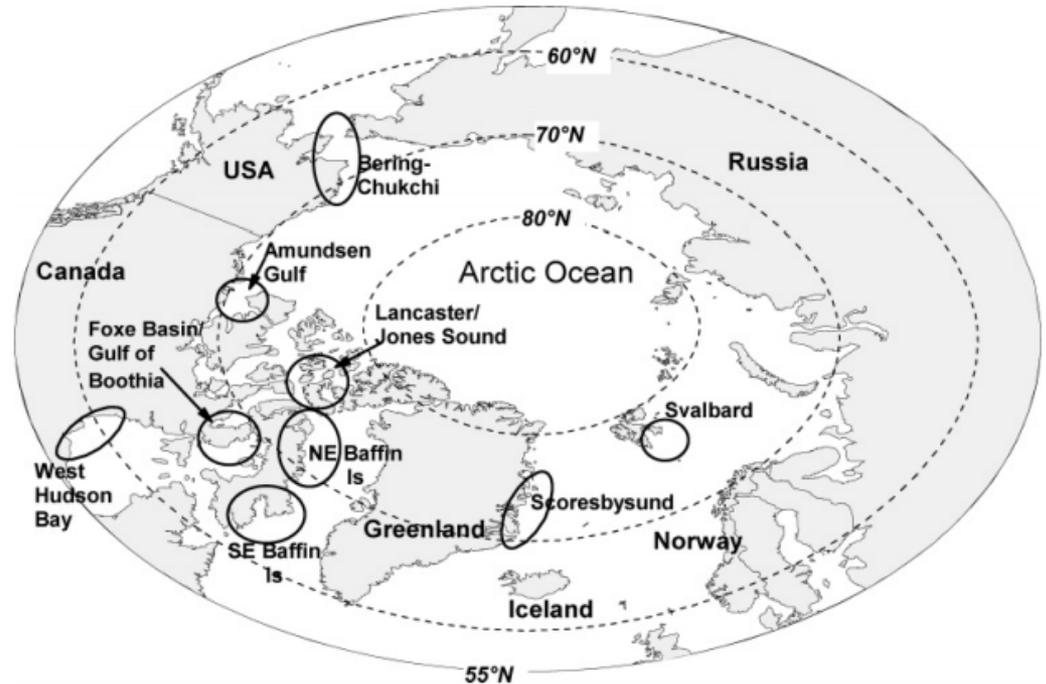
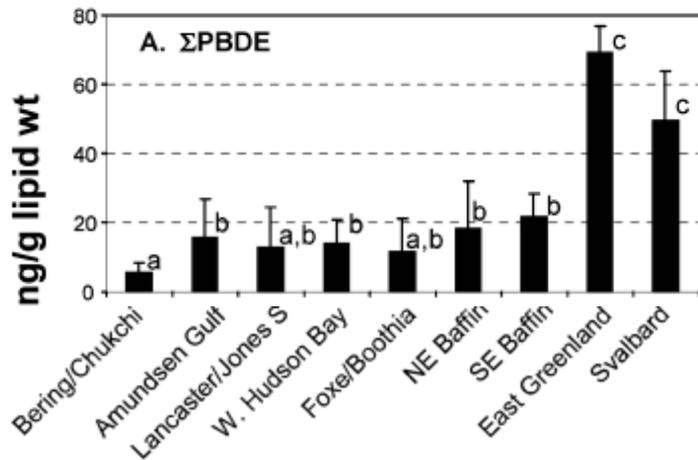
Transdermal Uptake of Diethyl Phthalate and Di(*n*-butyl) Phthalate Directly from Air: Experimental Verification



Indoor and outdoor connections

Brominated Flame Retardants in Polar Bears (*Ursus maritimus*) from Alaska, the Canadian Arctic, East Greenland, and Svalbard

Muir et al., 2006 *Environ Sci Technol*



- What do flame retardants in polar bears have to do with indoor air pollution??

Indoor and outdoor connections

Indoor Air Is a Significant Source of Tri-decabrominated Diphenyl Ethers to Outdoor Air via Ventilation Systems

Björklund et al., 2012 *Environ Sci Technol*

Table 4. Estimated Emissions of PentaBDE to Outdoor Air in Sweden (See SI for Full Description of Calculations and References)

source	emission factor	activity (kg/year)	annual emission (kg/year)	comment
metals manufacturing	35–716 $\mu\text{g}/\text{tonne}$ product	1.7×10^9	0.06–1	concerns the sum of 20 congeners (di-octaBDEs), with BDE-47 and -99 being the most predominant
municipal incineration	no information	0.8–18	not possible to estimate	
electronics recycling	no information	9×10^4 – 5.6×10^5	not possible to estimate	
e-waste fires	8.4–50.2 $\mu\text{g}/\text{kg}$ burnt material, assuming no extinguishing water	1.48×10^6	0.01–0.07	concerns sum of BDEs (47,85,99,100,138,153,154). nondetected congeners were assigned a value of 0 (d.l. = 1.5 $\mu\text{g}/\text{kg}$ burnt)
landfill fires	4.96 – 394 $\mu\text{g}/\text{kg}$ C burned	7×10^4 – 7×10^5	3.5×10^{-4} –0.028	concerns BDE-47 only
indoor environment - households	10–260 pg/m^3	1.7×10^{12} – 9.4×10^{12} m^3/year	0.024–0.92	concerns BDE-28, -47, -99, -153
indoor environment - public buildings	84–1600 pg/m^3	2.7×10^{12} – 8.7×10^{12} m^3/year	0.26–8.7	concerns BDE-28, -47, -99, -153
total			0.35–11	
percentage total contribution of indoor air			81–82	

For one of the first times we're aware of, indoor air pollution in modern countries is linked strongly to outdoor air pollution in remote regions of the world!

- Potential effects go beyond human beings

IAQ MEASUREMENT TECHNIQUES

Attribution: The majority of this material came from a 2012 graduate course at UT-Austin taught by Dr. Atila Novoselac, with help from Drs. Jeff Siegel, Neil Crain, and Richard Corsi

Motivation

- Throughout this course we've described a variety of indoor airborne pollutants
- Most can be categorized into:
 - Inorganic gases (e.g., O₃, CO, CO₂, NO_x)
 - Organic gases (e.g., VOCs, aldehydes, SVOCs)
 - Particulate matter
 - Mass
 - Number
- But we haven't discussed how to measure all of these yet

AEROSOL SAMPLING TECHNIQUES

Measuring particulate matter

- Sampling methods distinguish between:
 - Particle counting
 - No sizing
 - Particle sizing
 - Count + size information
 - Particle mass
 - Particle composition

For biological particles:

- Viable and non-viable bioaerosols

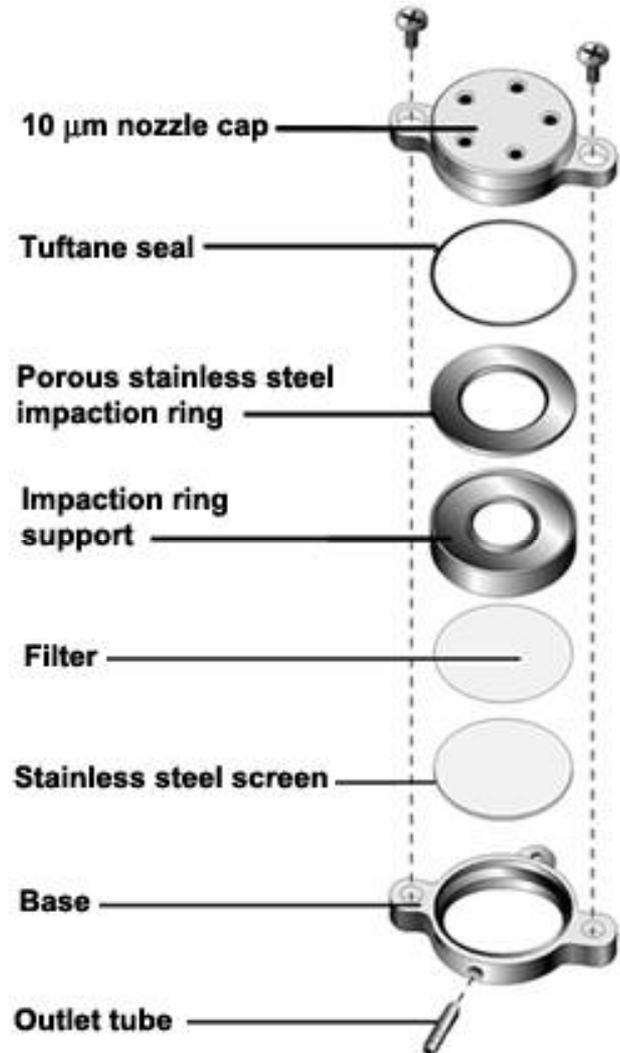
Gravimetric (mass-based) particle sampling

- Particles have very low masses
- Need to collect many particles to have measureable mass
- Most mass-based techniques are integrated samples
 - Sample onto filters at known airflow rate for known period of time
 - Weigh filters before and after
 - Calculate concentration
 - Correct for RH

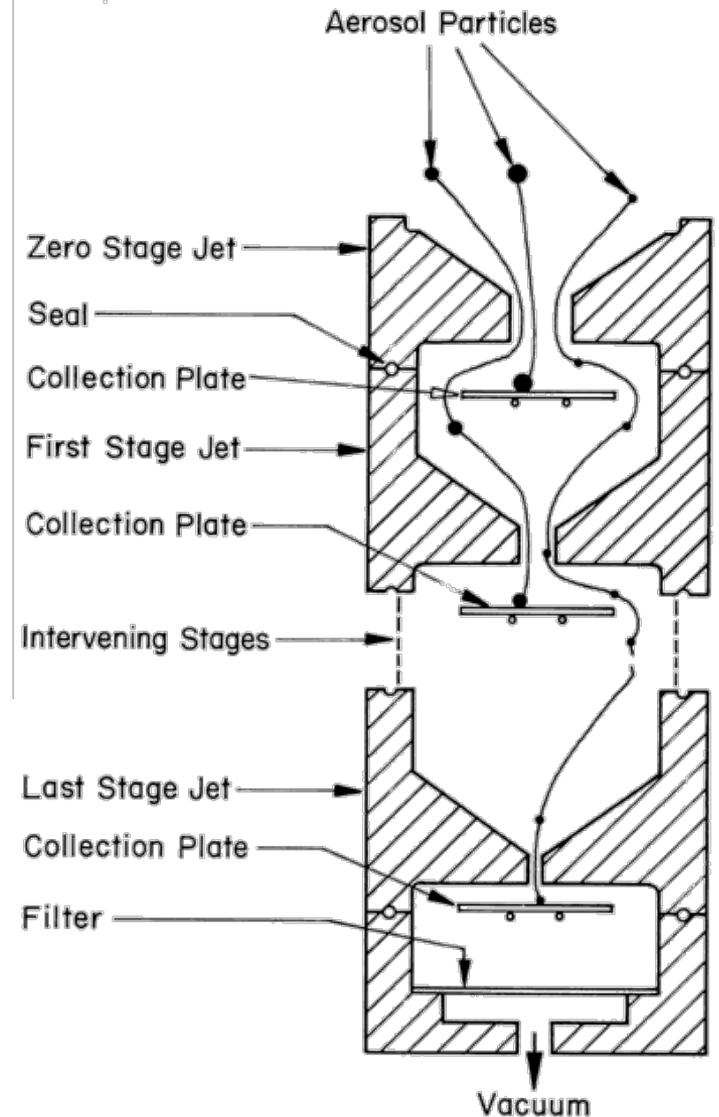
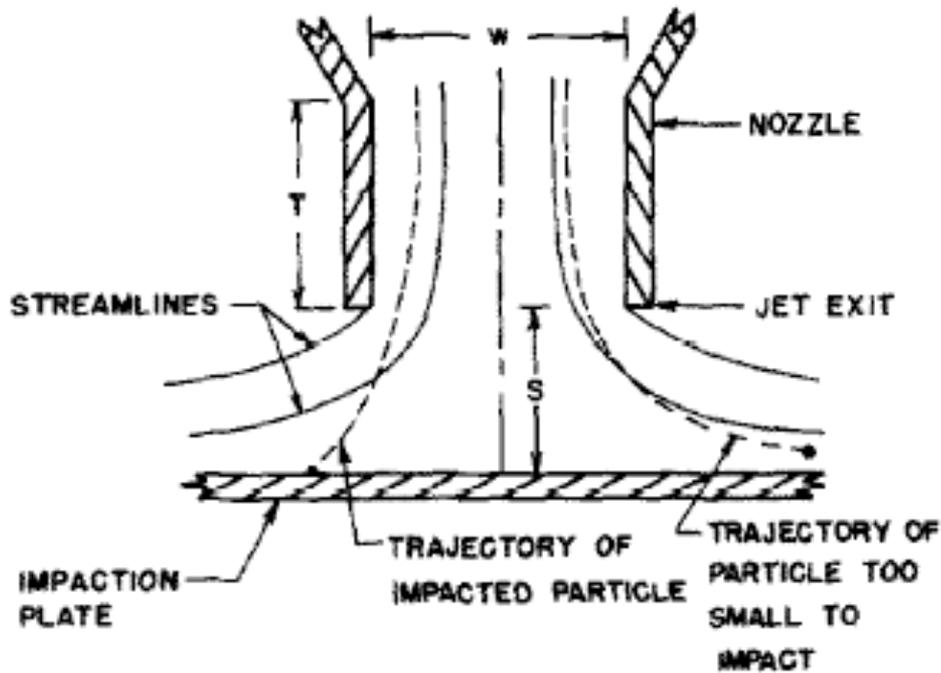
Particle Diameter [μm]	Particle Mass [g]
0.01	$5 \cdot 10^{-19}$
0.1	$5 \cdot 10^{-16}$
1	$5 \cdot 10^{-13}$
10	$5 \cdot 10^{-10}$

Gravimetric (mass-based) particle sampling

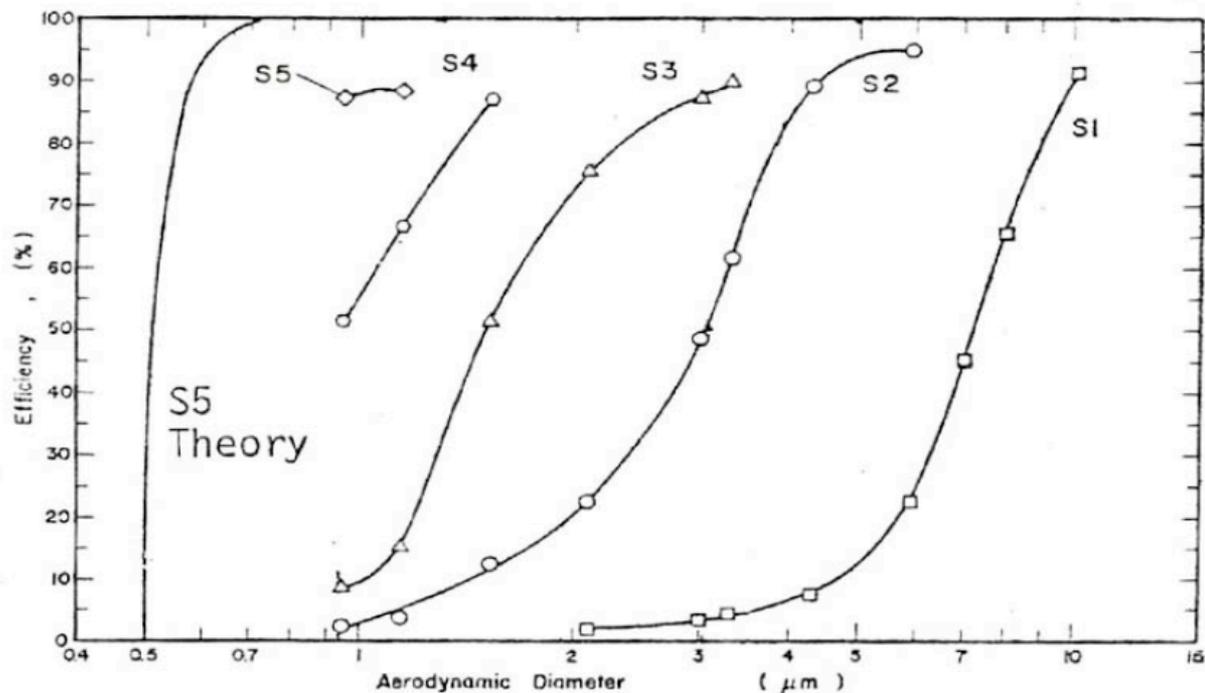
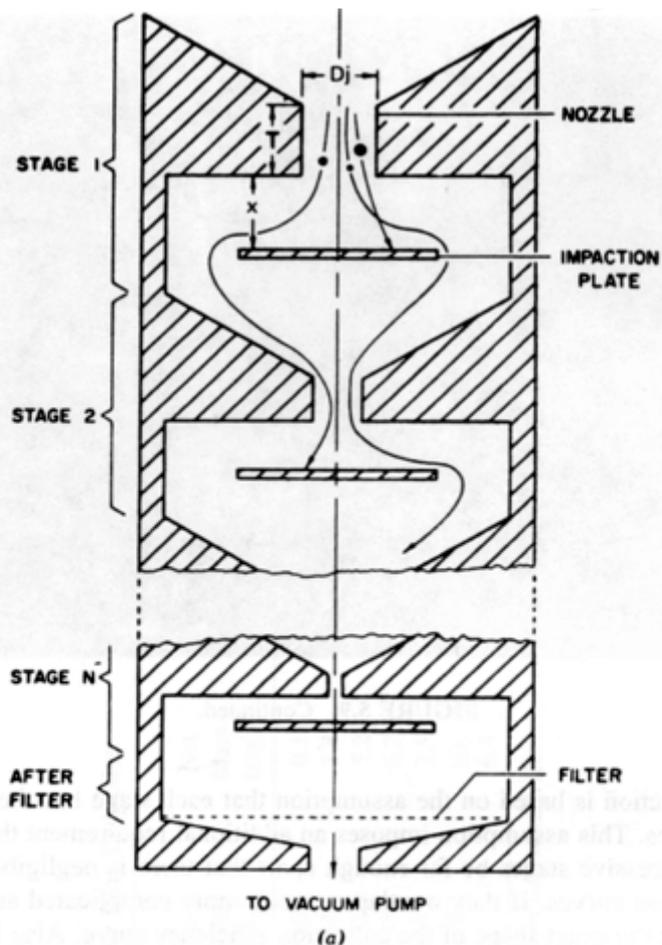
SKC PEM sampler



Gravimetric particle sampling: Cascade impactor



Gravimetric particle sampling: Cascade impactor



Bioaerosol sampling

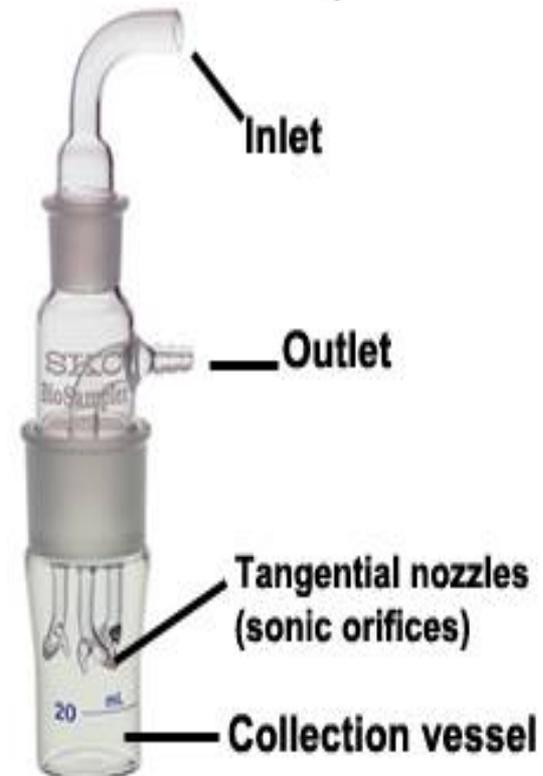
- **Impactors**

- Collect on filter, extract DNA from filter
- Advantages and disadvantages of various filters



- **Impingers**

- Collect aerosol in liquid suspension



Bioaerosol sampling

	Sampling rate	Size resolved sampling	Viability	Sample Suitable for molecular methods	Advantages/disadvantages
	Sampling rate	Size resolved sampling	Viability	Sample suitable for molecular methods	Advantages/disadvantages
<p>Cascade impactors</p> <p><u>Mechanism:</u> The sampling air stream makes a sharp bend and particles are stripped based on their aerodynamic diameter.</p> <p><u>Typical models:</u> -Anderson Cascade Impactor; -MOUDI cascade impactor; -BGI 900 L/min high volume cascade impactor.</p>	Typically 10 to 28 L/min. Some samplers allow for > 500 L/min.	Provides the best size distribution information. Different models offer between 1 and 12 stages for collecting aerosols with aerodynamic diameters from 10 nm to >18 µm.	Only at 28 L/min collection rates and requires direct sampling onto agar plates.	Stages can be covered with filters, membranes, or plates and samples can then be extracted from these materials.	<p><u>Advantages:</u></p> <ul style="list-style-type: none"> -Best ability to define particle size distributions; -Models available to perform culturing;\. <p><u>Disadvantages:</u></p> <ul style="list-style-type: none"> -High cost per sampler, especially for high volume samplers; -Sampling inefficiencies due to particle bounce; -Not sensitive as total sampled mass is divided among multiple stages.

Bioaerosol sampling

	Sampling rate	Size resolved sampling	Viability	Sample Suitable for molecular methods	Advantages/disadvantages
<p>Liquid impingement</p> <p><u>Mechanism:</u> Sampled air is passed through a small opening and captured into a liquid medium.</p> <p><u>Typical Models:</u> -SKC swirl impingers; -Omni 3000 high volume impinge.</p>	14 L/min for glass impingers, new high volume models are capable of >100 liters per minute.	Very limited information on the size ranges that are collected. Efficiency drops in low volume glass impingers below aerodynamic diameters of 1 µm. High volume samplers have not been characterized for sampling efficiencies as a function of particle sizes.	Impingers are flexible since organisms are impinged into liquid media or buffer and can be used for culturing or molecular analysis.	Samples are impinged into 10 to 20 ml of liquid, which may require concentration by filtration.	<p><u>Advantages:</u></p> <ul style="list-style-type: none"> -Sample is collected into liquid and does not require extraction from a solid collection medium; -Low cost of low flow glass impingers. <p><u>Disadvantages:</u></p> <ul style="list-style-type: none"> -Limited information on efficiencies, and the particle sizes that are sampled; -High volume impingers are high cost; -Glass impingers suffer from low sampling rate and limited sampling times due to evaporation; -High volume impingers have complex systems for collecting the sample and rewetting surfaces, and there is large concern about effectively decontaminating the equipment.

Optical measurements

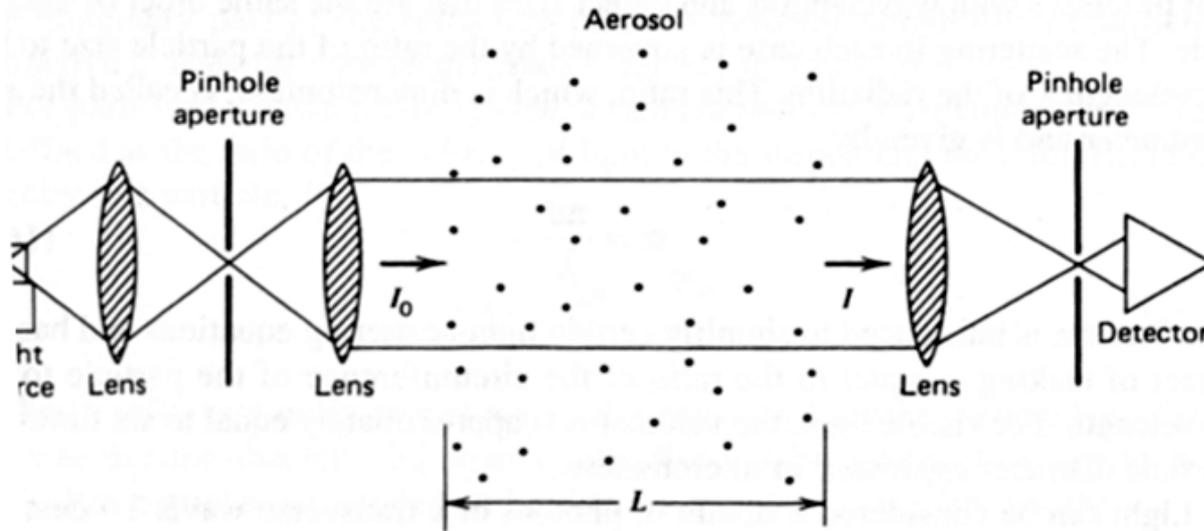


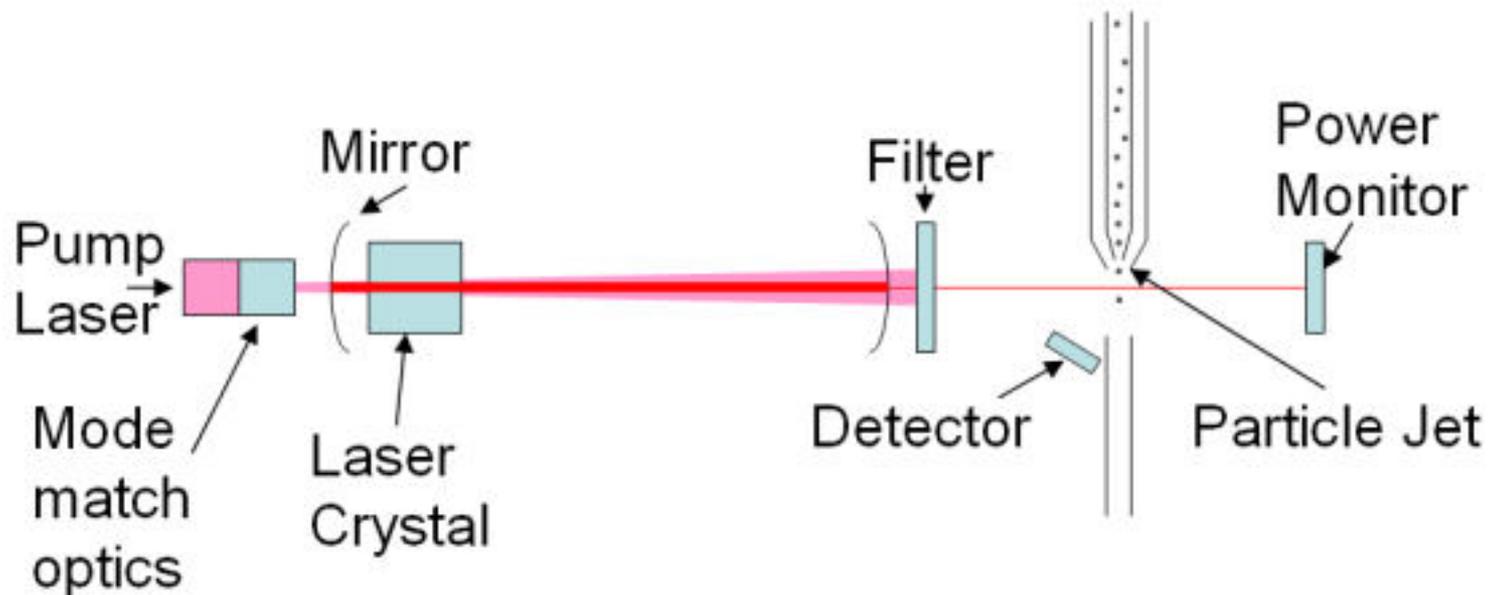
FIGURE 16.1 Schematic diagram of an extinction-measuring apparatus.



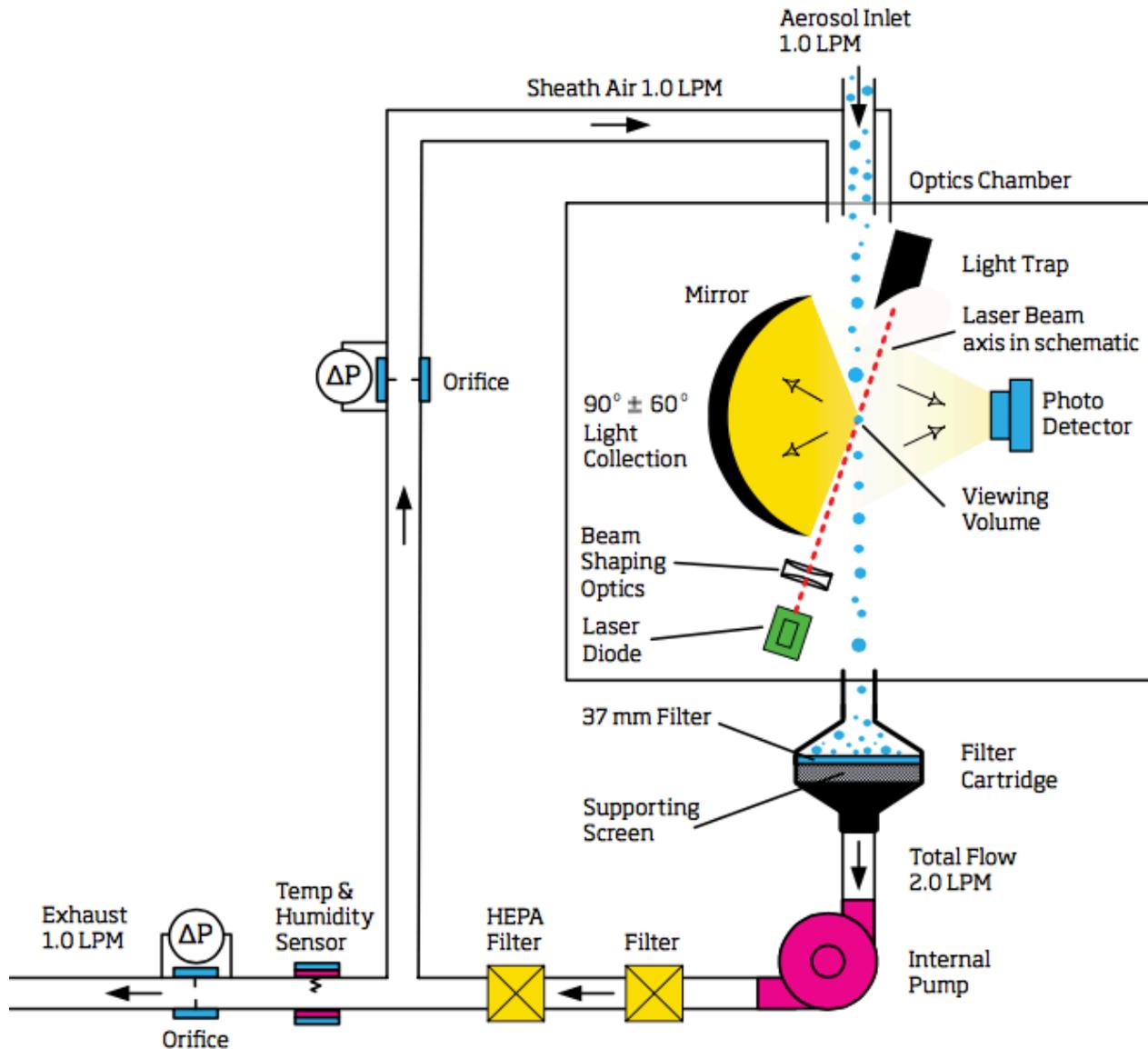
Extinction:
$$\frac{I}{I_0} = e^{-\sigma_e L}$$

Optical particle counter

- Similar to photometer, but particles are isolated
 - May require dilution
- 0.065 – 20 μm
 - Practically 0.1 – 5 μm
- Some devices just count and don't size



Optical measurements



Optical measurements: Mie/Rayleigh Theory for Scattering

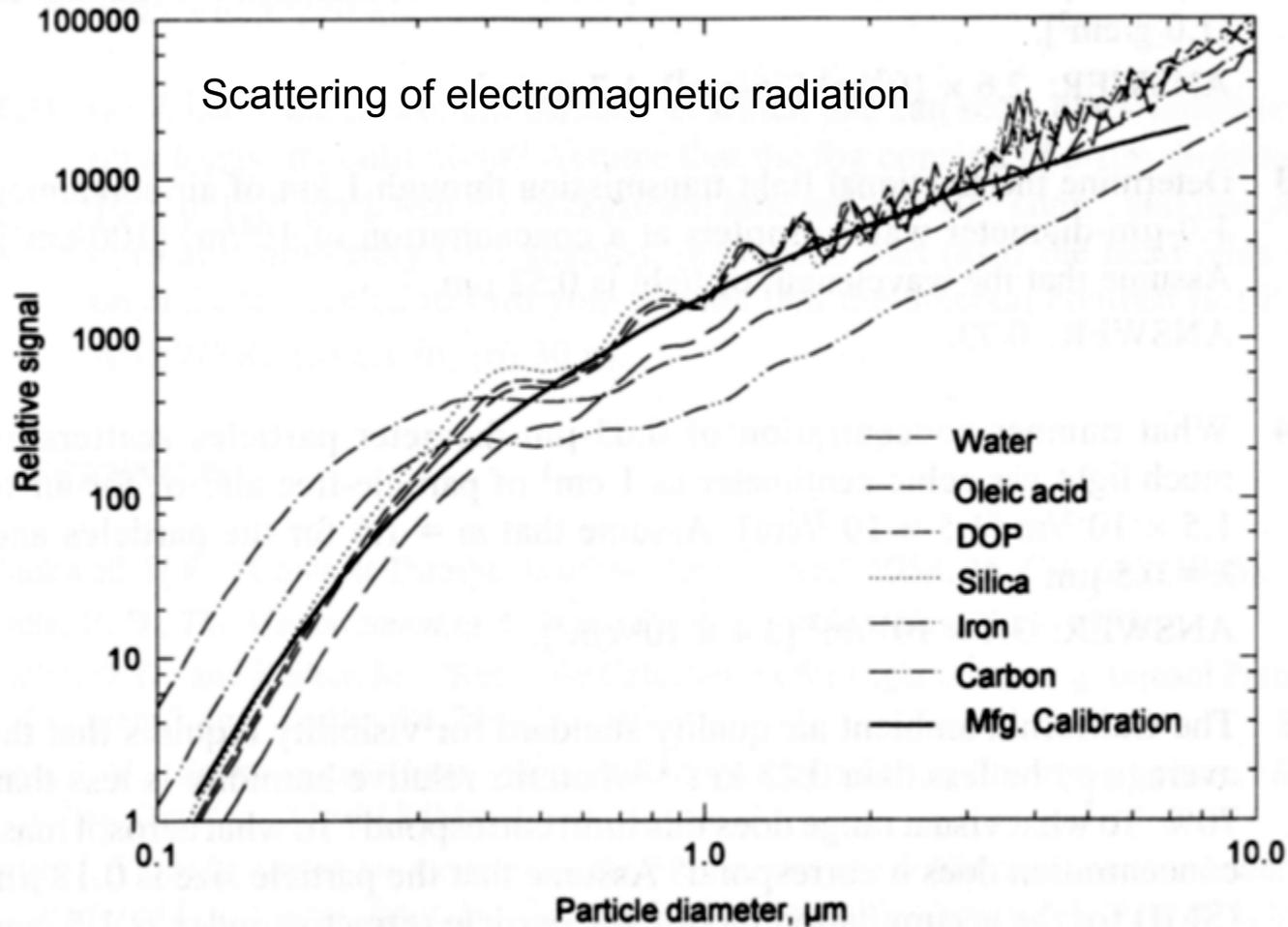


FIGURE 16.16 Calculated response curves for six materials and manufacturer's calibration curve for model LAS-X[®] (PMS, Inc., Boulder, CO) optical particle counter.

Measuring particle “mass” optically

- Photometers
 - Typically **relative** instruments
 - Sensitive to particle speed



- Nephelometer
 - Measure scattering for aerosol sample (~ 1L) over wide range of angles (θ)
 - Particle density is function of the light reflected into the detector
 - Scattered light depends on properties of the particles such as their shape, color, and reflectivity
 - Determines mass concentration much more accurately than photometer
 - Often calibrated to single particle composition

Condensation nuclei counter (CNC)

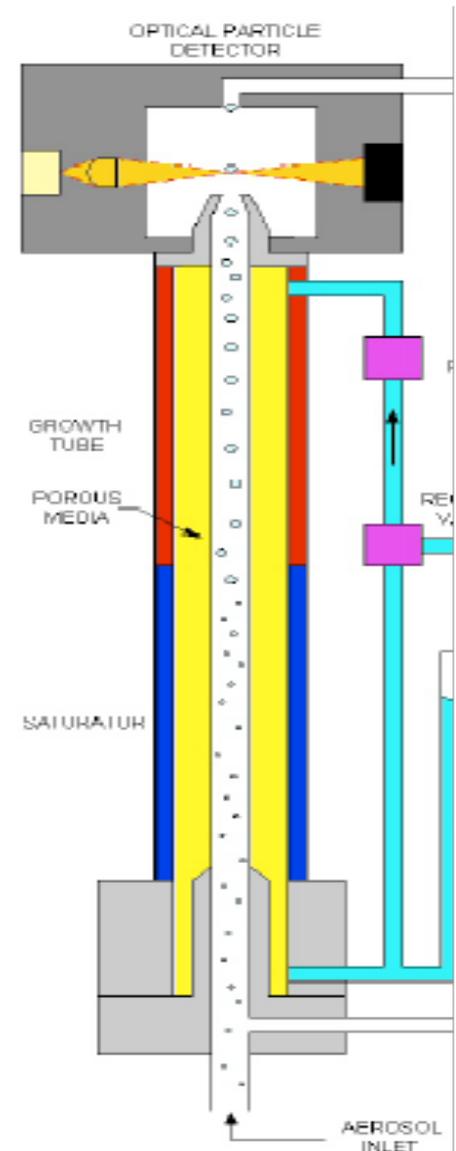
- Subject aerosol stream to alcohol (or water) vapor
- Cool air stream to cause condensation
- Count particles with an optical particle counter

- Closely related to a condensation particle counter (CPC)

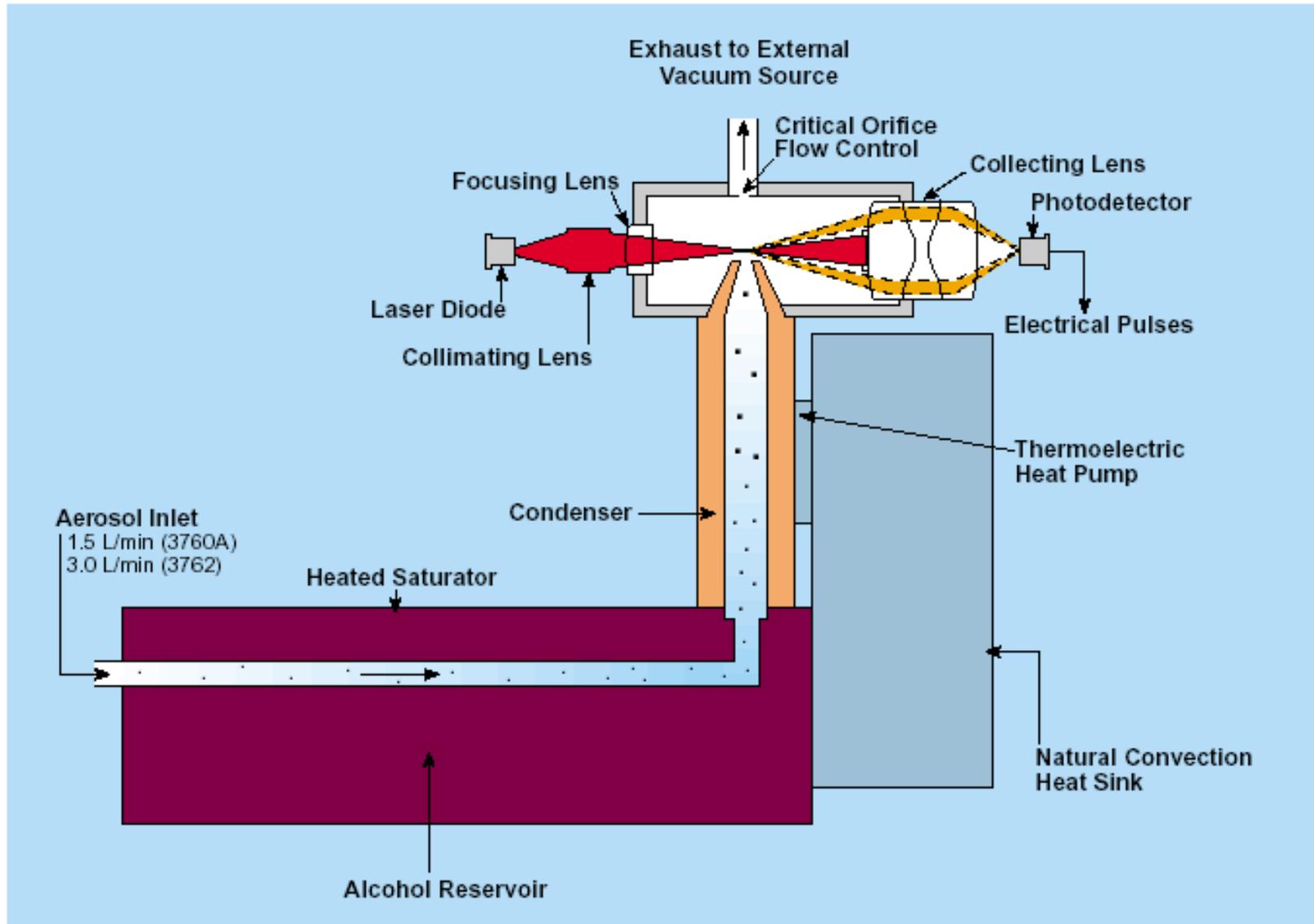


Condensation nuclei counter (CNC)

- Particles are passed through a wick and grown with either water or butanol
 - Aerosol stream saturated and temperature equilibrated
 - Heterogeneous condensation on condensation nuclei (the particles)
 - Grown to 2 to 3 micrometers
 - Individual particles passed through light beam and scatter light onto a photodetector

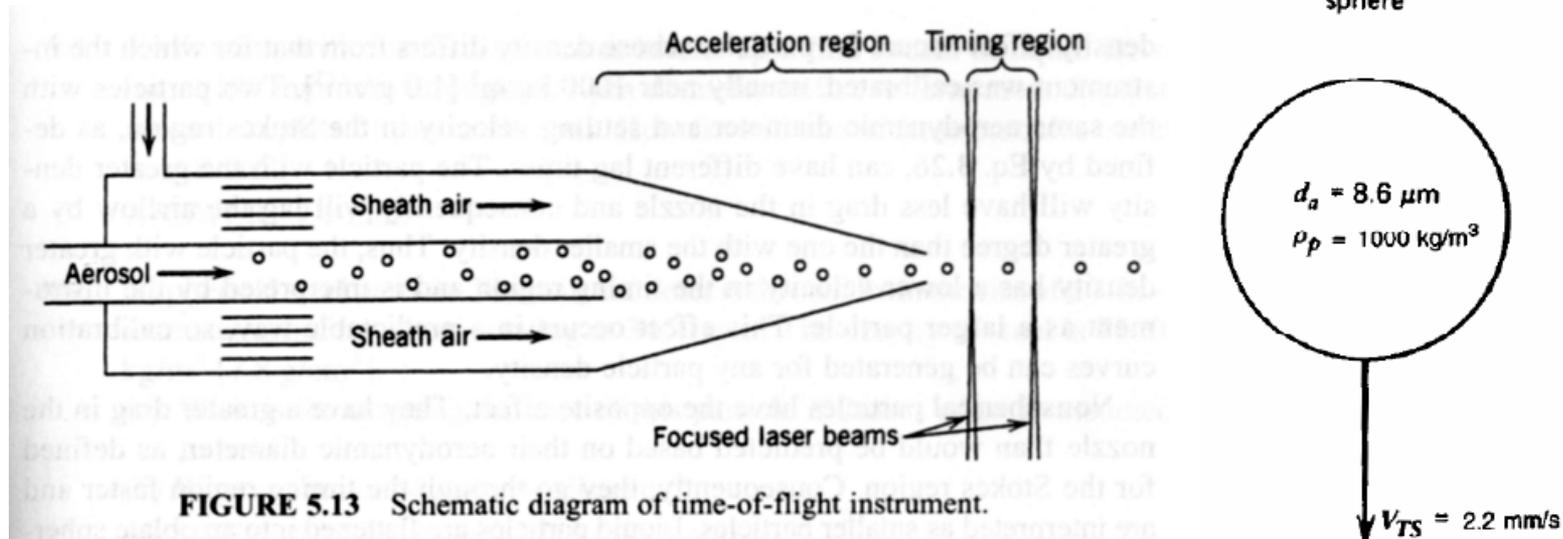


Condensation nuclei counter (CNC)



Aerodynamic particle sizer

- One of many **time-of-flight** instruments
 - Two laser beams separated by known distance
 - Particle is accelerated between beams
 - Time between beams being broken is calibrated to a test aerosol
 - Particles exiting the jet have a velocity related to their aerodynamic diameter (assume spherical particles and unit density)
- Measures 0.5 - 20 μm



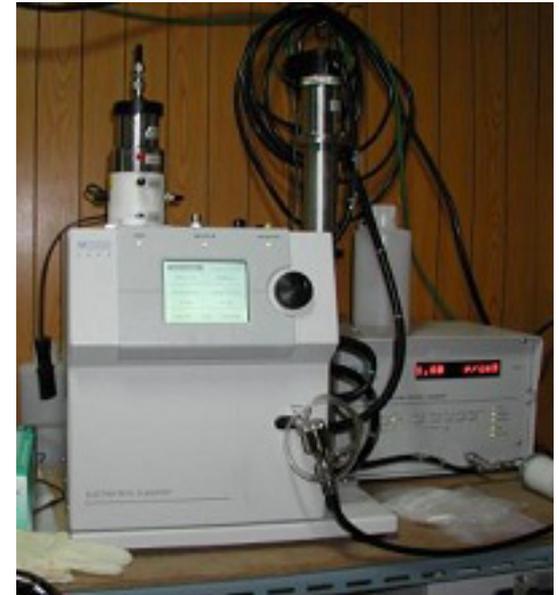
Aerodynamic particle sizer

- Small particles move at the air velocity
- Large particles lag air velocity
- Problems
 - Small particles not-Stokesian
 - Larger density is sized as a larger particle
 - Shape also influences drag
 - Multiple particles in sizing chamber (same as other devices)



Particle mobility analyzer

- Particles entering the system are neutralized using a radioactive source
 - Yields equilibrium charge distribution
- Particles then enter a Differential Mobility Analyzer (DMA) where the aerosol is classified according to **electrical mobility**
 - Only particles of a narrow range of mobility exit through the output slit.
- This monodisperse distribution then goes to a Condensation Particle Counter which determines the particle concentration at that size
- Measures 0.001 – 1 μm
 - 0.002 – 0.4 μm most accurate



Electrical mobility:
Ability of charged particles to move through medium in response to electric field (inversely proportional to diameter)

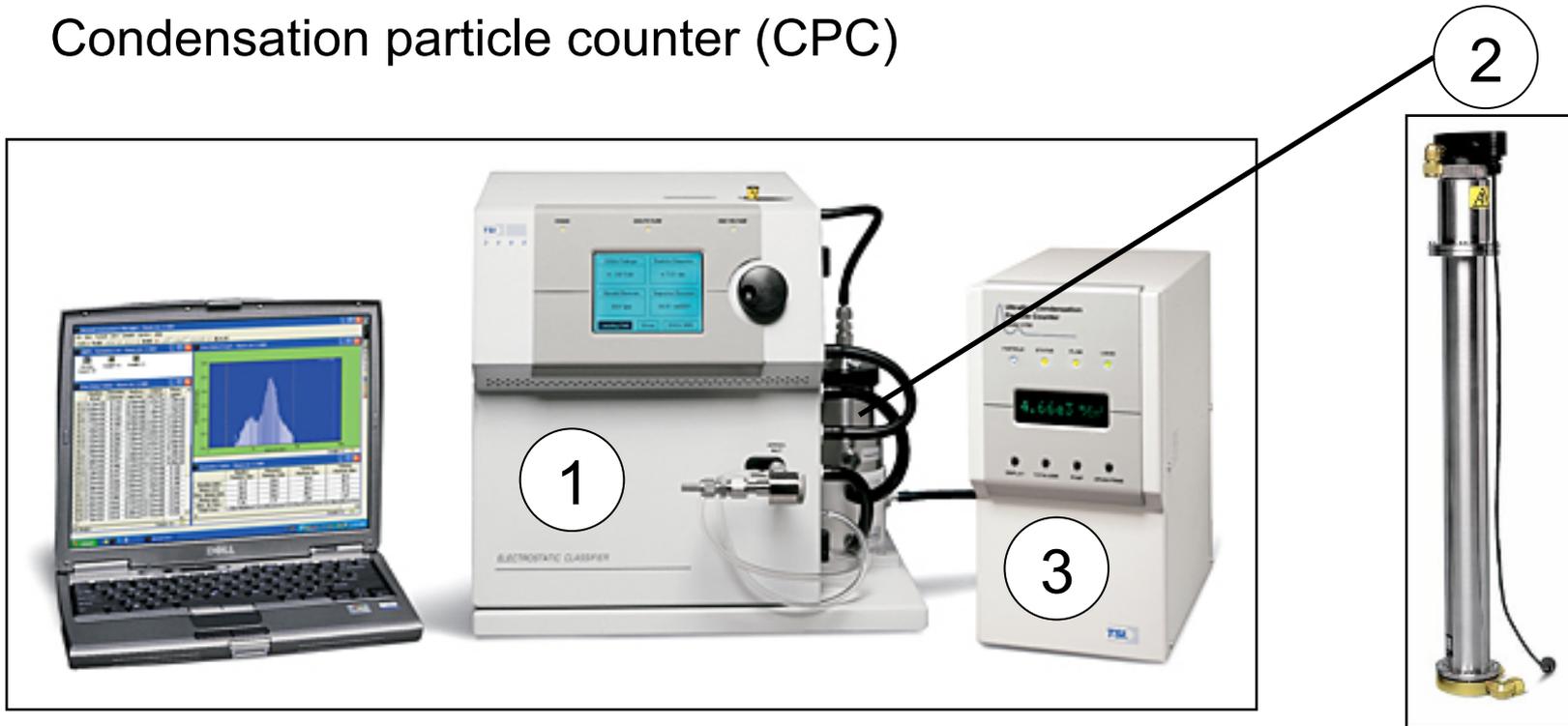
Particle mobility and charge distributions

TABLE 15.4 Distribution of Charge on Aerosol Particles at Boltzmann Equilibrium

Particle Diameter (μm)	Average Number of Charges	Percentage of Particles Carrying the Indicated Number of Charges								
		< -3	-3	-2	-1	0	+1	+2	+3	>+3
0.01	0.007				0.3	99.3	0.3			
0.02	0.104				5.2	89.6	5.2			
0.05	0.411			0.6	19.3	60.2	19.3	0.6		
0.1	0.672		0.3	4.4	24.1	42.6	24.1	4.4	0.3	
0.2	1.00	0.3	2.3	9.6	22.6	30.1	22.6	9.6	2.3	0.3
0.5	1.64	4.6	6.8	12.1	17.0	19.0	17.0	12.1	6.8	4.6
1.0	2.34	11.8	8.1	10.7	12.7	13.5	12.7	10.7	8.1	11.8
2.0	3.33	20.1	7.4	8.5	9.3	9.5	9.3	8.5	7.4	20.1
5.0	5.28	29.8	5.4	5.8	6.0	6.0	6.0	5.8	5.4	29.8
10.0	7.47	35.4	4.0	4.2	4.2	4.3	4.2	4.2	4.0	35.4

Scanning Mobility Particle Sizer (SMPS)

1. Electrostatic classifier (EC)
2. Differential mobility analyzer (DMA)
3. Condensation particle counter (CPC)



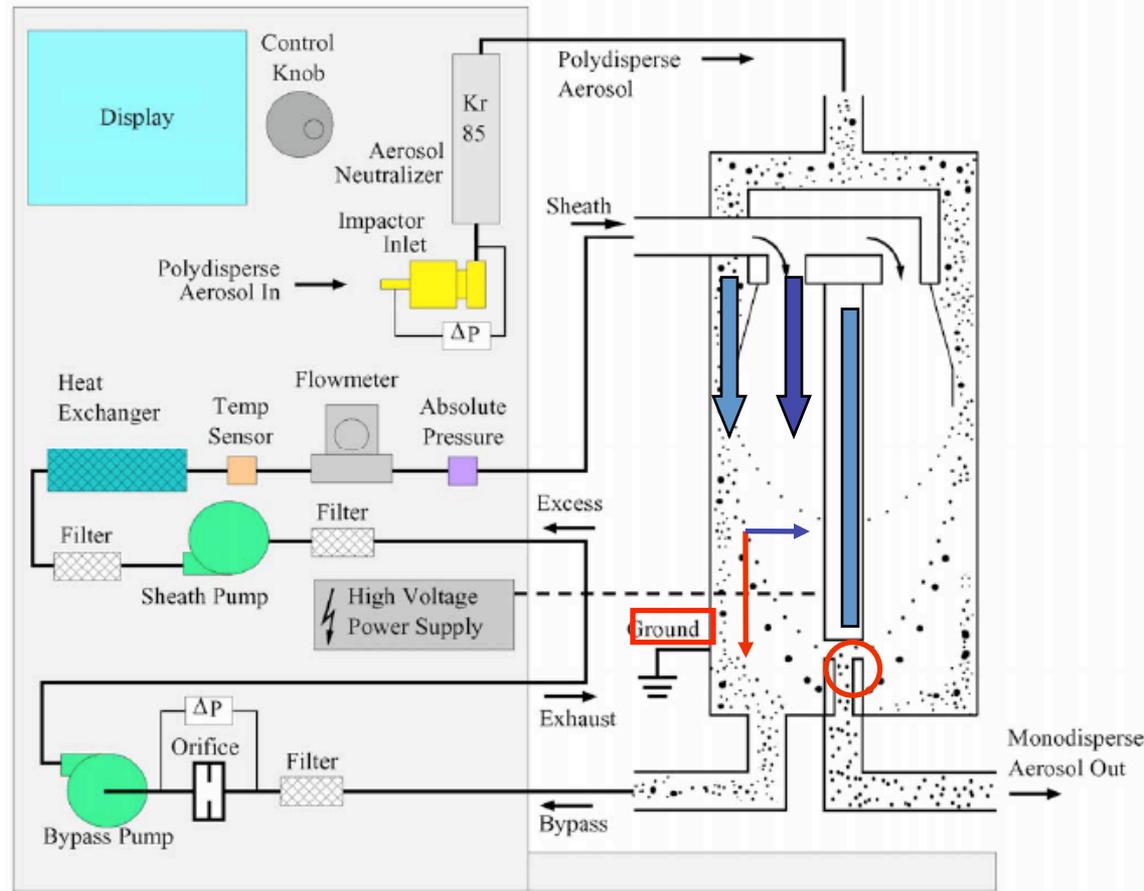
SMPS: EC and DMA

EC

- Kr-85 bipolar charger

DMA

- 2 laminar flows
 - Sheath and aerosol
- 2 concentric cylinders
 - Center negative voltage
 - Electric field
- **Positive** particles attracted through sheath air
- Location depends on electrical mobility, flow rate, and geometry
 - Cycles through different voltages to capture different size particles



Cost of particle sensors

- Relatively inexpensive
 - Gravimetric for particle mass
 - Light scattering for large particle mass
 - Condensation nucleus counter (CNC) for counting small particles
 - Cascade impactor for size-resolved mass
- Mid-range
 - Optical particle counters
- Expensive
 - Aerodynamic particle sizing for large particles
 - Differential mobility analyzer for small particles

Other issues with particle measurements

- Sampling line losses
 - Generally an issue for large ($>1 \mu\text{m}$) and small ($< 0.05 \mu\text{m}$) particles
- Sampling particles in moving air stream
 - Isokinetic and non-isokinetic sampling
- Particle composition
 - Collect sample of particles on filter
 - Analyze as you would for liquid or solid compounds
 - SMPS or APS w/ mass spec
 - Very expensive
- Bioaerosol sampling
 - Fungi, bacteria, viruses
 - Quantitative or presence/absence
 - Culturable, viable, DNA-based
 - Inhibitors

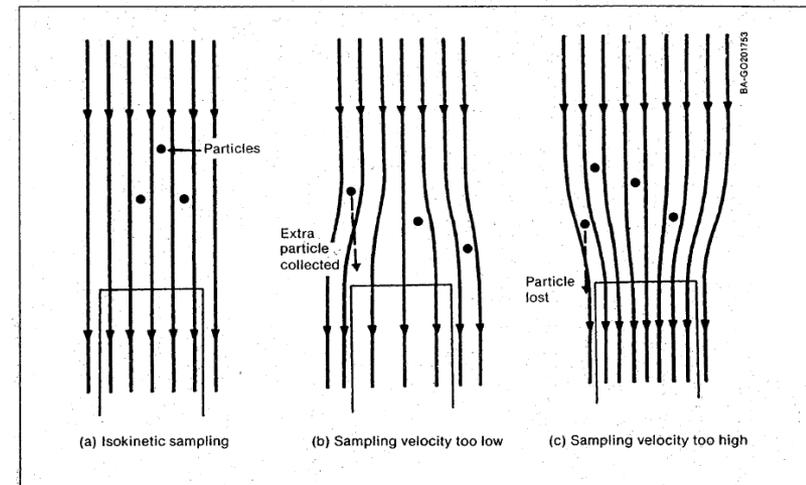


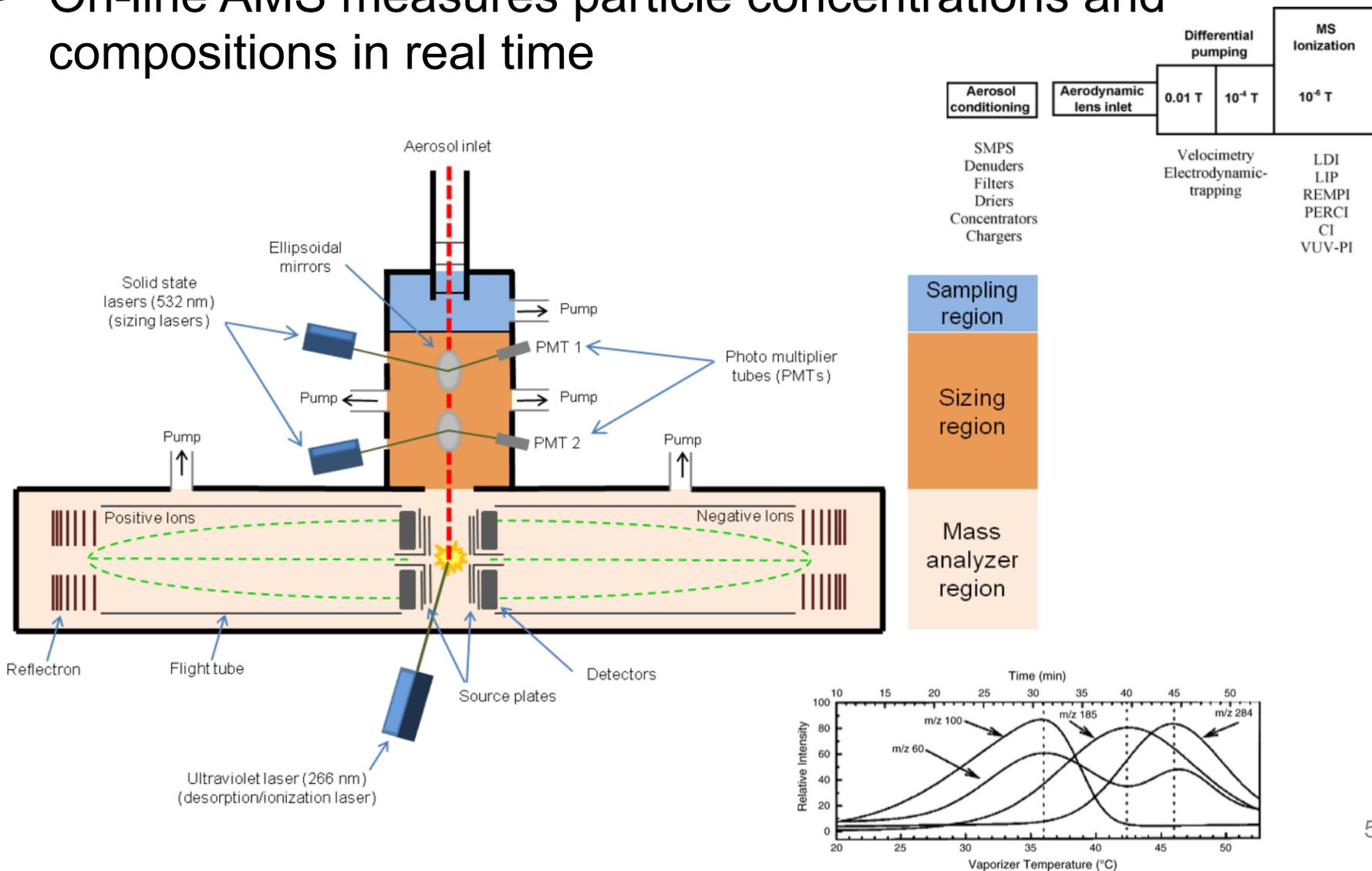
Fig. 7-10. Gas stream lines at the entrance to sampling probes (Source: Adapted from Strauss 1975, Fig. 2.12. © 1975. Used with permission of Pergamon Press)

Aerosol mass spectrometry (AMS)



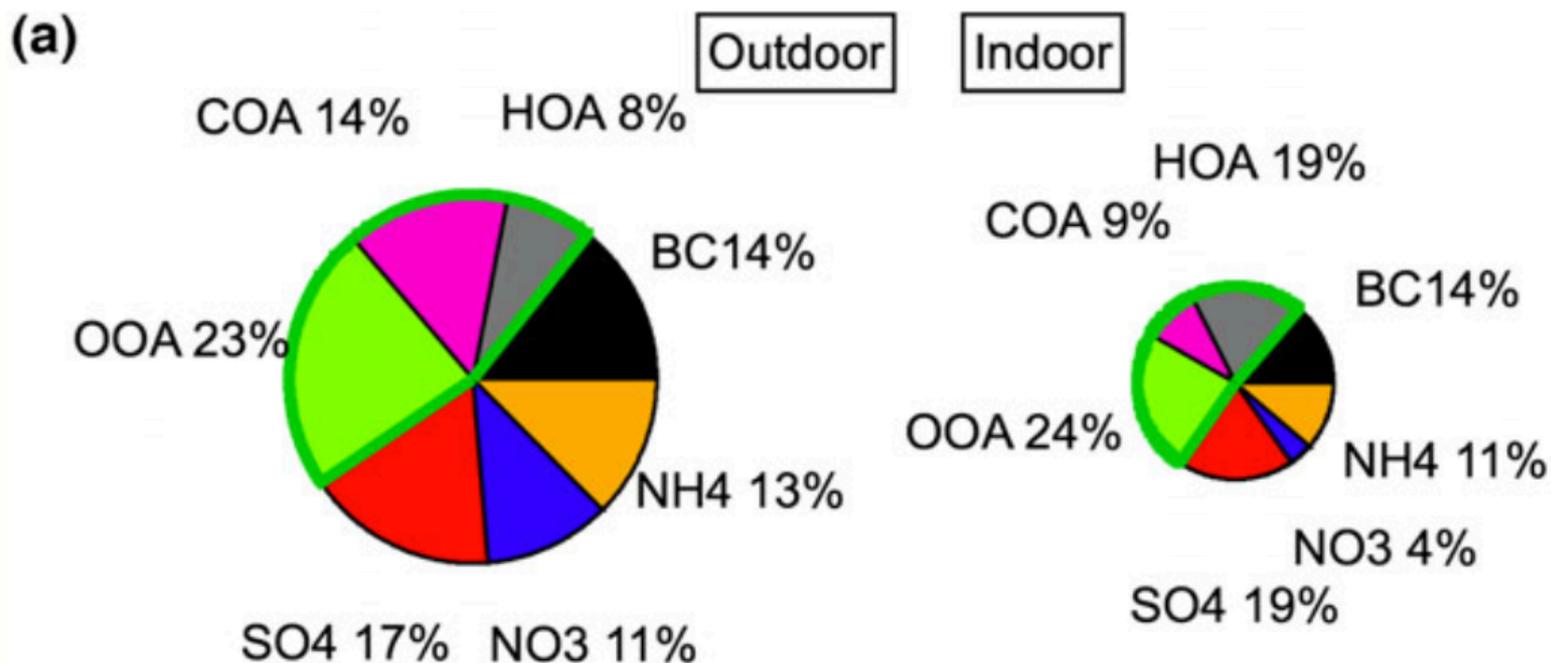
Aerosol mass spectrometry (AMS)

- On-line AMS measures particle concentrations and compositions in real time



Indoor AMS measurements

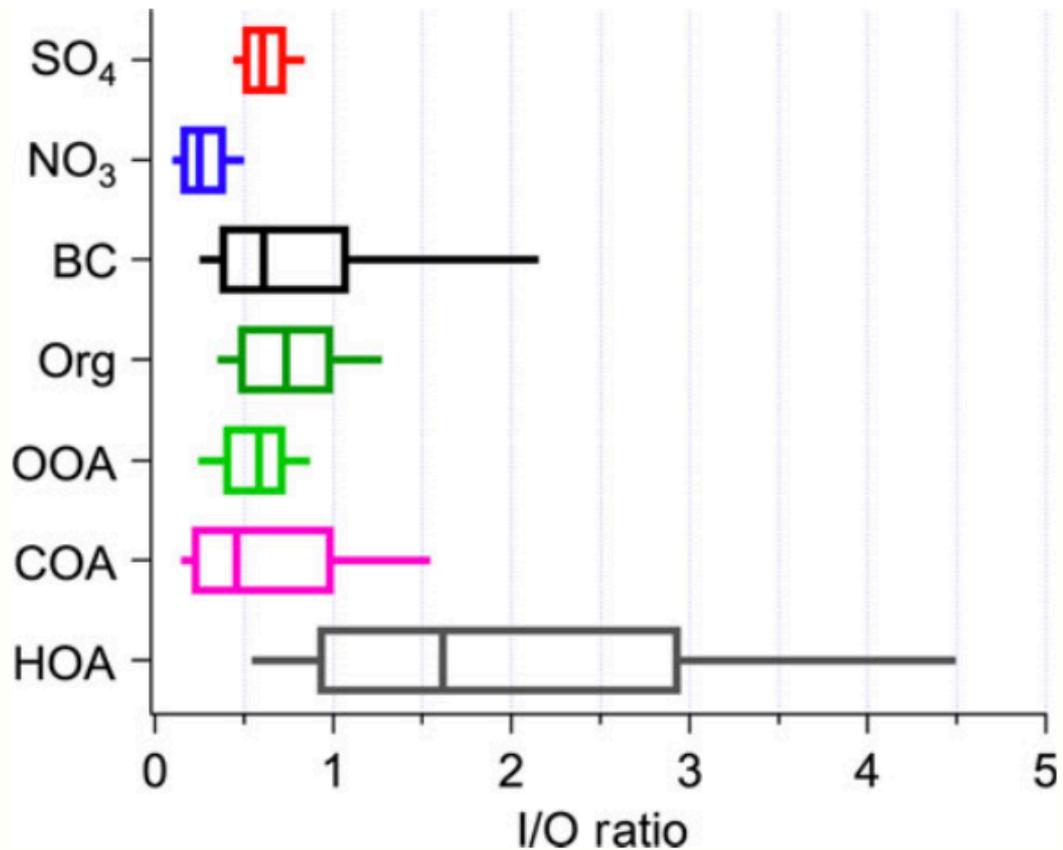
Real-time transformation of outdoor aerosol components upon transport indoors measured with aerosol mass spectrometry



SO_4 = sulfate aerosol; NO_3 = nitrate aerosol; BC = black carbon; Org = total organic aerosol (OA); OOA = oxygenated OA; COA = cooking OA; and HOA = hydrocarbon-like OA.

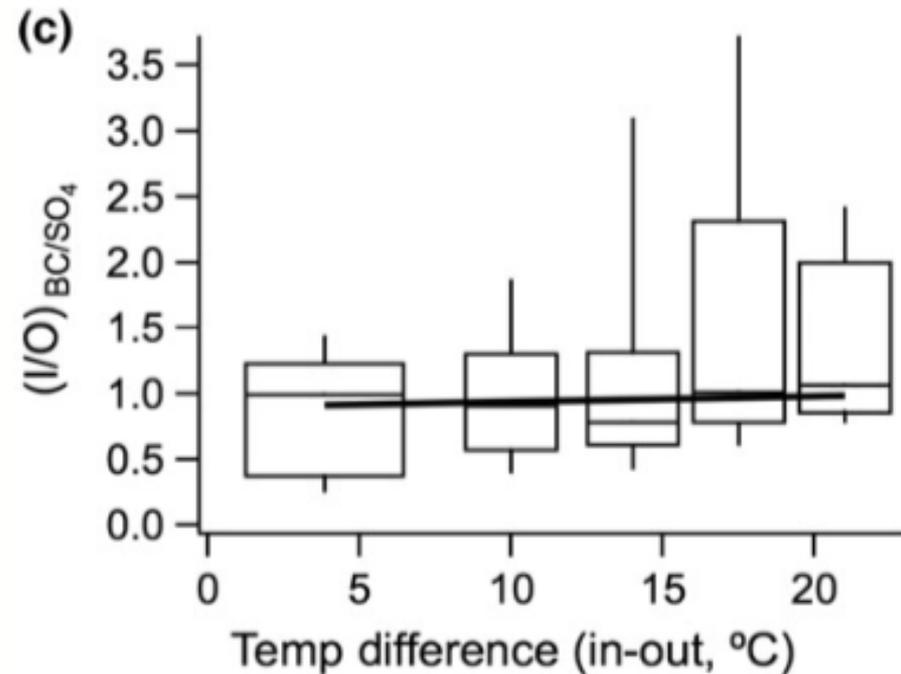
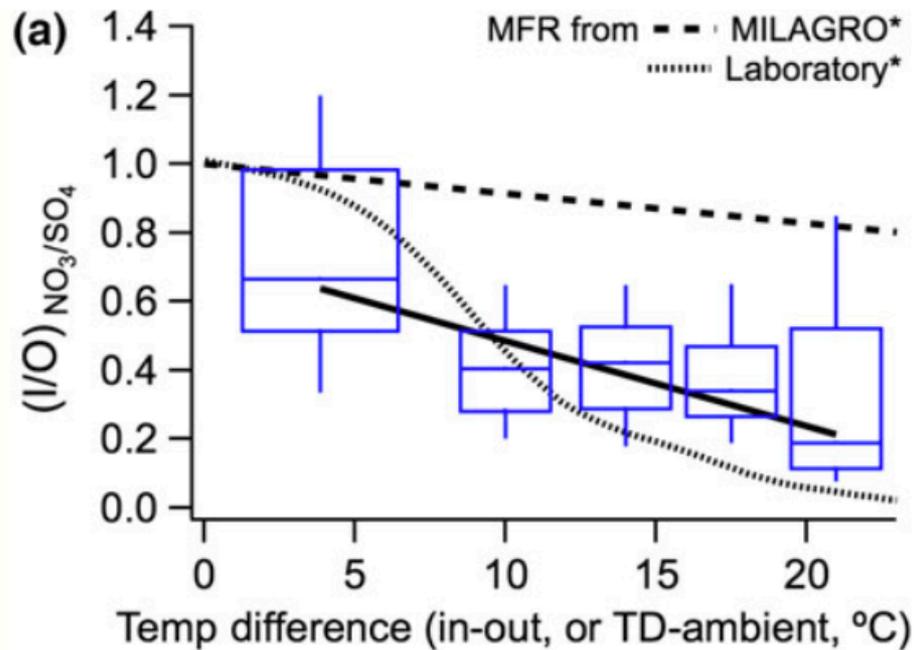
Indoor AMS measurements

Real-time transformation of outdoor aerosol components upon transport indoors measured with aerosol mass spectrometry



Indoor AMS measurements: Phase-change

Real-time transformation of outdoor aerosol components upon transport indoors measured with aerosol mass spectrometry



Summary of particle measurements

- Wide variety of instruments available for particle measurement
 - What size of aerosol are you interested in?
 - Do you need sizing or is counting sufficient?
 - Do you need real-time data?
 - What type of aerosol are you trying to measure?
 - How much accuracy do you need?
 - How much money do you have?

MEASURING INORGANIC GASES

CO, CO₂, NO_x, and O₃

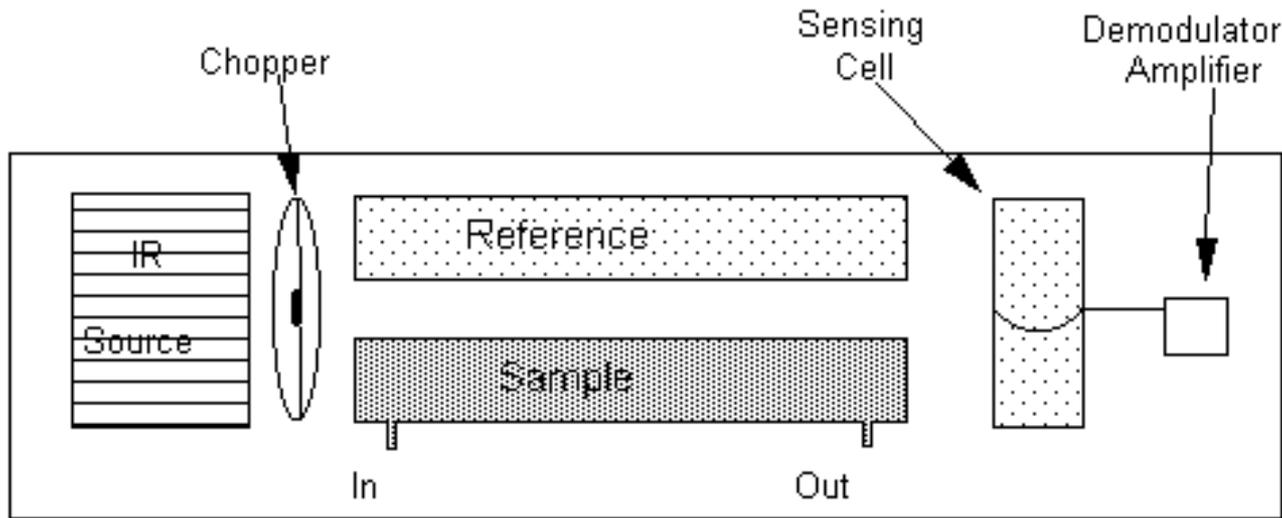
Techniques for measuring CO

- Electrochemical (common for hand held or home devices)
 - Two electrodes
 - Oxidize CO to CO₂ → generates electric current
- Biomimetic (gel cell)
 - Synthetic hemoglobin – darkens in presence of CO (color change)
- Semiconductor (wires of tin dioxide / ceramic base)
 - CO reduces resistance
 - Works for high CO concentrations
- Non-Dispersive Infrared Detection (NDIR)
 - Relies on absorption band (similar for other instruments, e.g. CO₂)

Techniques for measuring CO₂

- Non-dispersive infrared (NDIR) → most common
- Electrochemical (reduce CO₂ → generate current)
- Photoacoustic (CO₂ absorbs light energy → measure pressure change)
 - Photoacoustic effect relates pressure change to CO₂ conc.
- Potentiometric (CO₂ into solution – changes pH)
- Gas chromatography w/ MS or TCD
 - High sensitivity
 - High cost

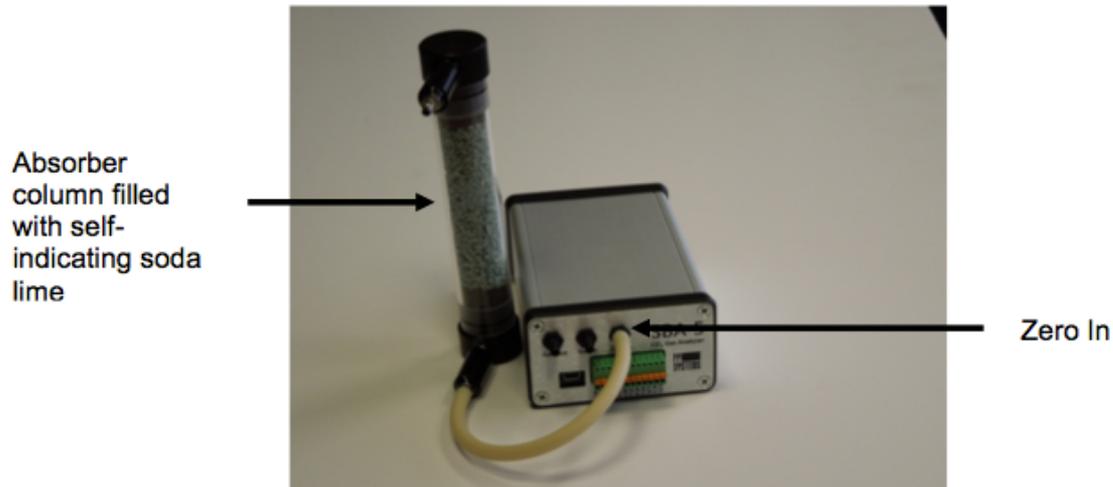
Non-dispersive infrared (NDIR)



- Measures the infrared light absorbed by CO₂ as it passes through a flow-through IR absorption cell
 - CO₂ peak absorbance @ 4.3 μm (higher CO₂, higher absorption)
 - Possible interference from other species (H₂O, CO)
 - Interferences from other IR-absorbing gases are minimized by use of a highly wavelength-specific detector

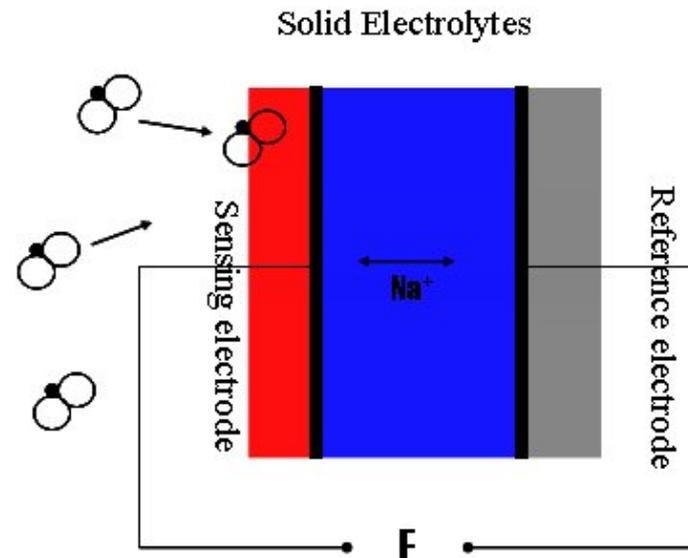
Dealing with interference and NDIR

- PP Systems SBA-5 CO₂ analyzer
- IR beam at 4.26 μm (similar to light bulb)
- Positioned at one end of a tube with a sensor sensitive to photons at 4.26 μm at the other end
- The cell absorbs CO₂ and the sensor reading decreases
- New feature: auto-zero w/ soda lime



Electrochemical sensing

- CO₂ diffuses into the sensor through a porous membrane to the working electrode
 - Causes electrochemical reaction, oxidizes the target gas
- This reaction results in an electric current that passes through the external circuit



Ozone measurements: Diffusion badges

- Personal diffusion badges
 - Diffusion-based; chemical coating
 - The principle component of the coating is nitrite ion, which in the presence of ozone is oxidized to nitrate ion on the filter medium
 - $\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$
 - After sample collection, the filters are extracted with ultrapure water and analyzed for nitrate ion by ion chromatography
 - Useful for inexpensive, long-term samples



Ozone measurements: UV absorbance

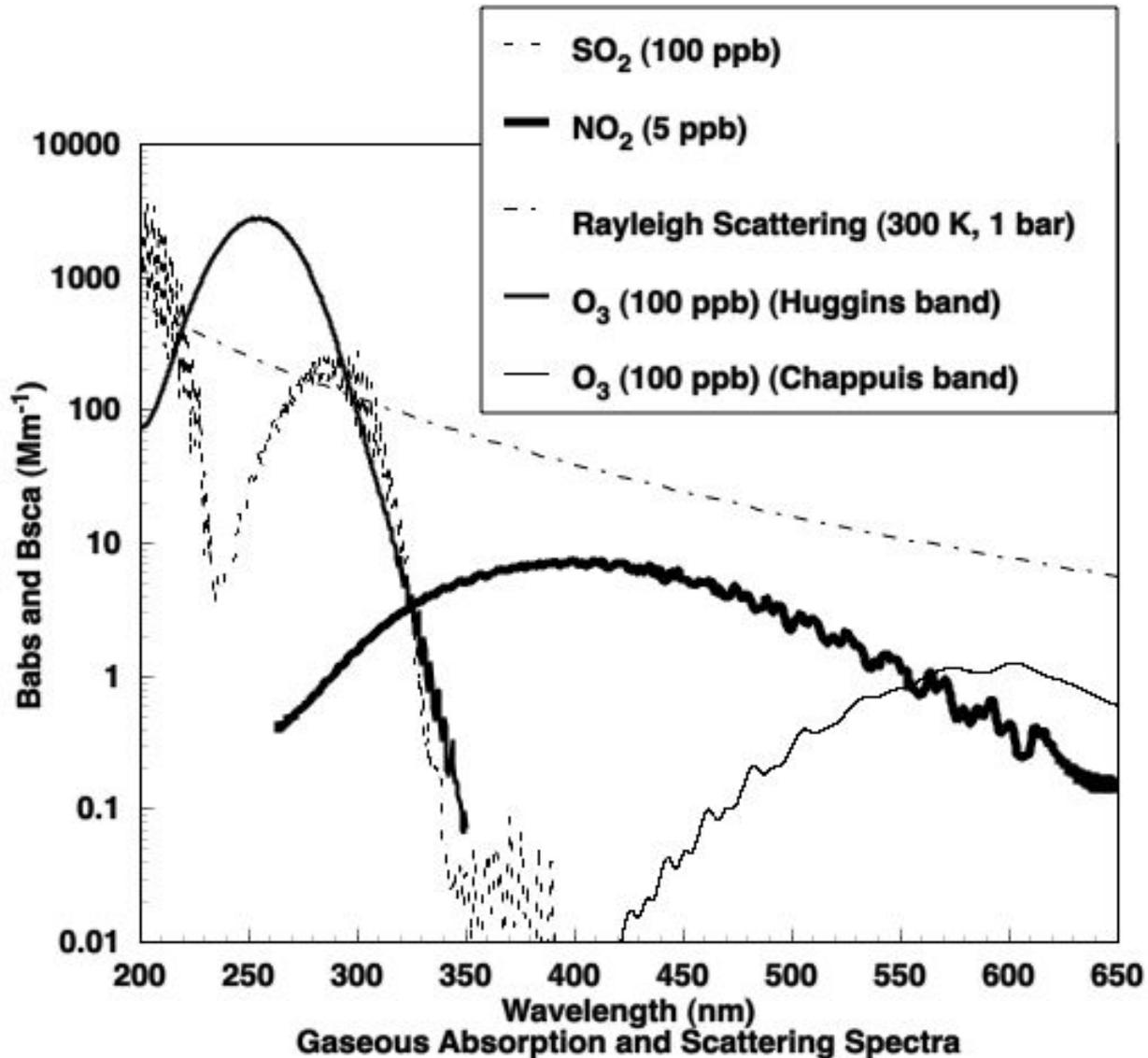
UV example: 2B Technologies Model 205



- Measure ozone by comparing transmission of light through a detection cell (ozone peak absorbance at 254 nm)
 - UV, not IR
- Light intensity measurements are made with ozone present and with ozone removed
 - Ozone measured using Beer-Lambert Law

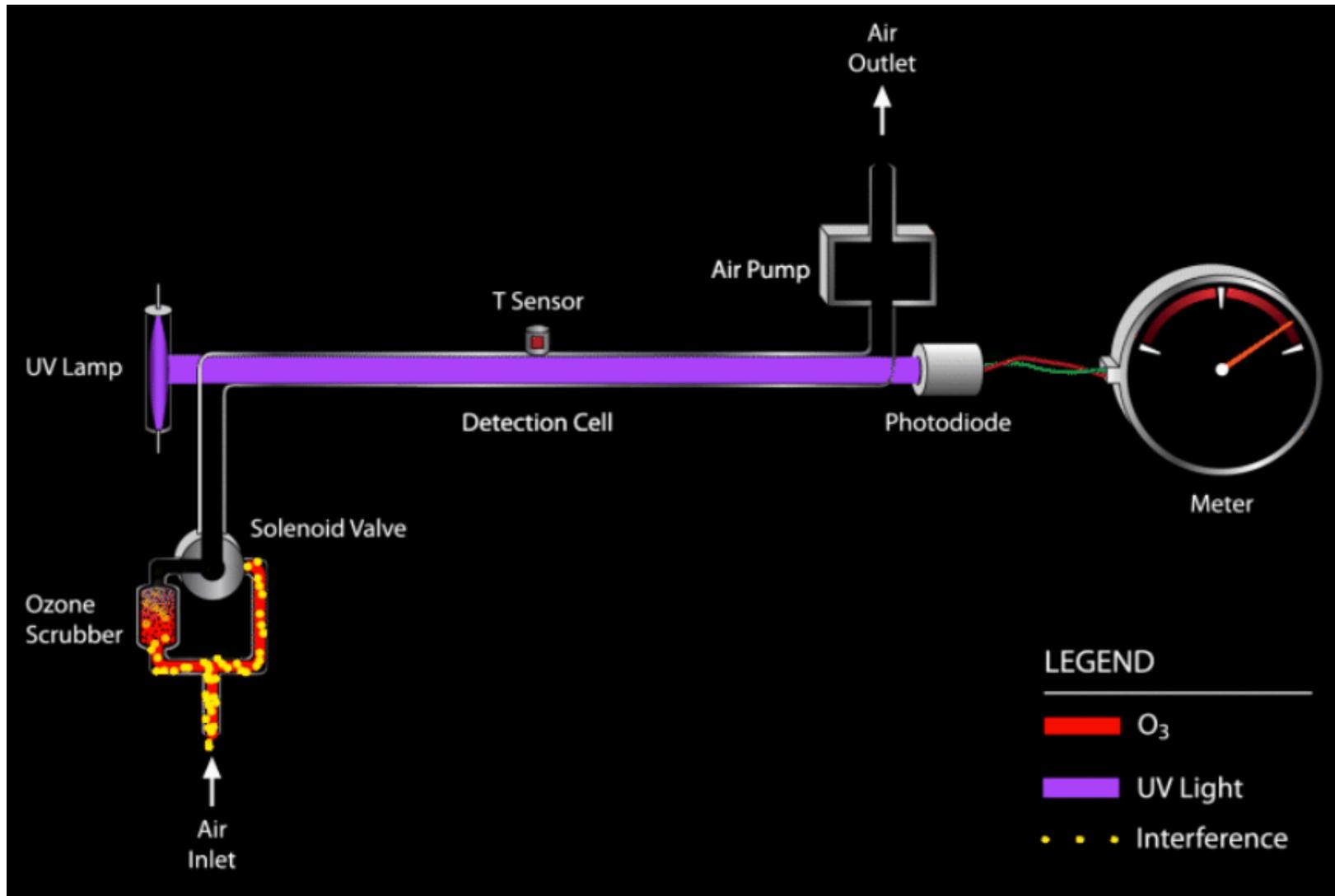
$$T = \frac{I}{I_0} = e^{-\Sigma \epsilon l} = e^{-\epsilon l c}$$

UV absorbance of O₃, NO₂, and SO₂



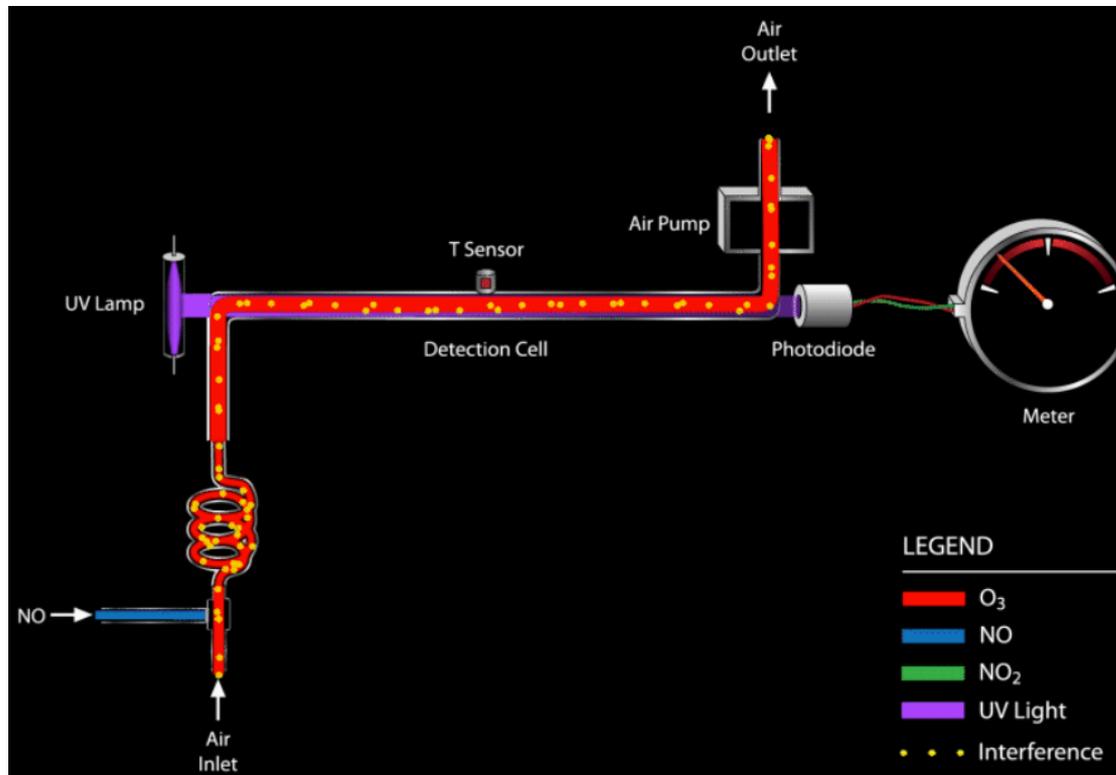
Ozone measurements: UV absorbance

UV example: 2B Technologies Model 205



Ozone measurements: UV absorbance

UV example: 2B Technologies Model 211 (“scrubber-less”)

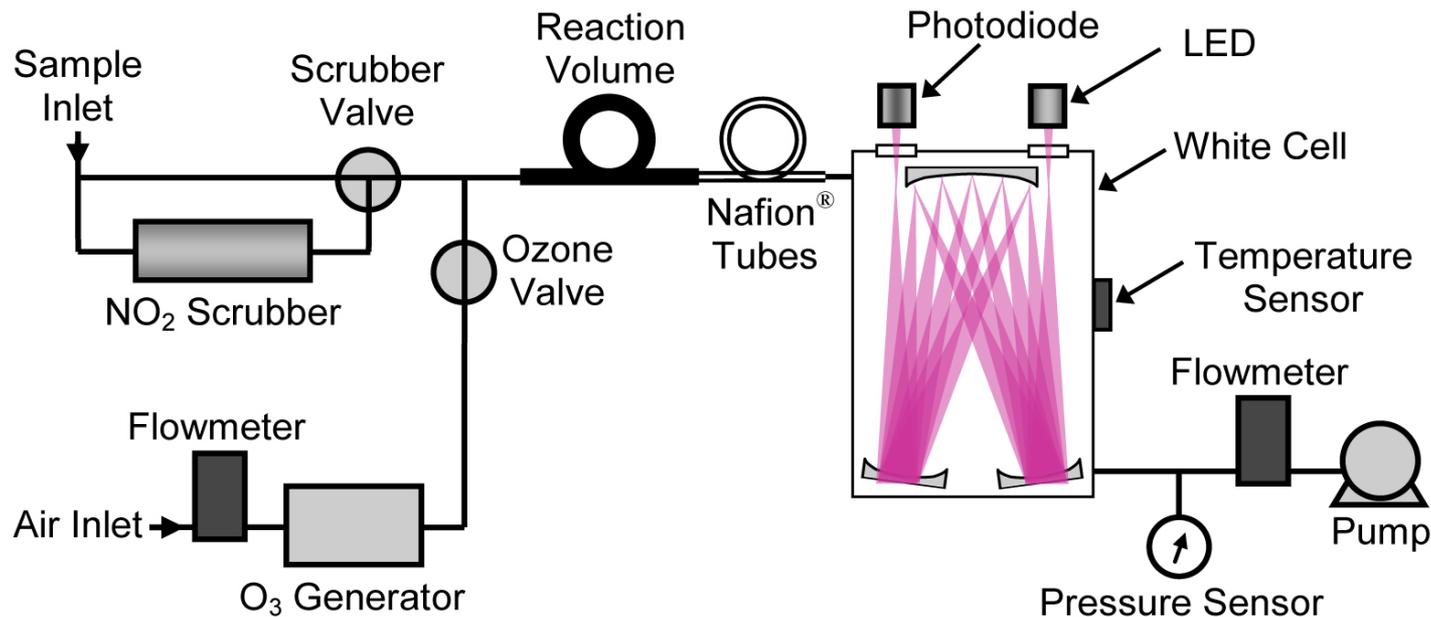
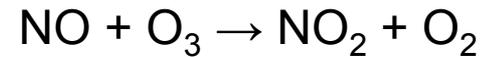


NO_x measurements: UV

- UV example: 2B Technologies Model 405
- Measures NO_x = NO + NO₂



- NO₂ is measured using absorbance at 405 nm
- NO is measured by 100% conversion of NO with O₃
 - Measured by bypassing NO₂ scrubber and measuring light intensity with and without adding O₃ to convert NO to NO₂

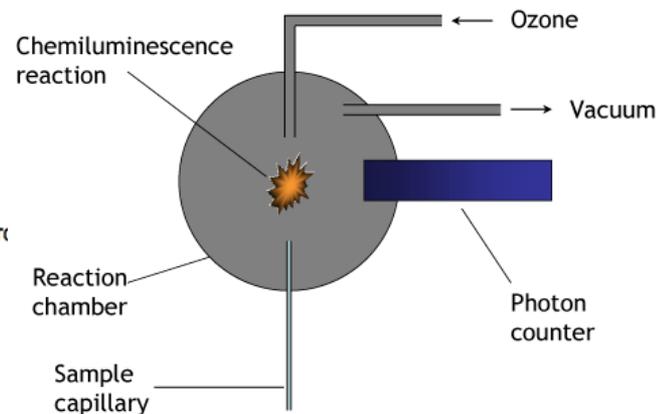
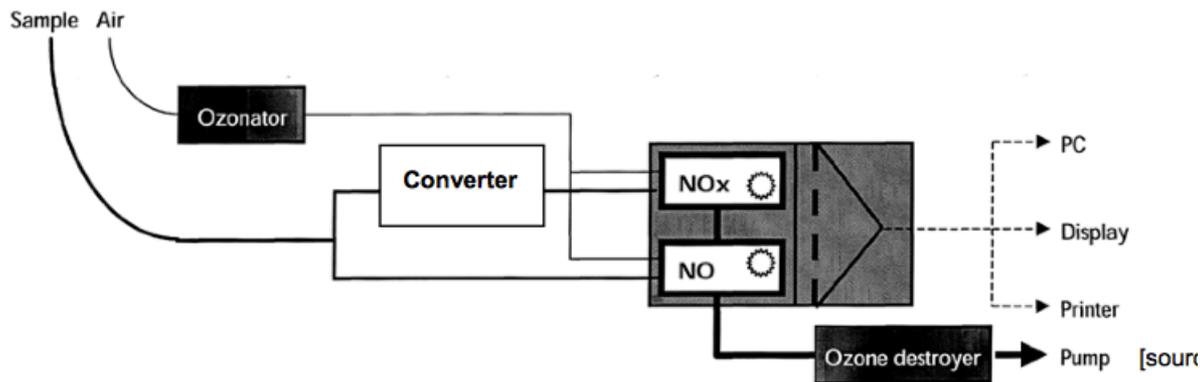


NO_x measurements: Chemiluminescence

- Reaction between NO and O₃ emits light
- Photons produced are detected by a photo multiplier tube
 - Output voltage is proportional to NO concentration



Nitrogen monoxide + Ozone ==> Nitrogen dioxide + Oxygen



MEASURING ORGANIC GASES (VOC AND SVOC)

Sample Collection Methods

- Two methods:

1. Real-time measurement/analysis

- Generally has a sensor (mostly FID, PID)
- Some have separation (w/ GC) + sensor
- Also: colorimetric tubes (general: MDL > 1 ppm)



2. Collect air sample for laboratory analysis

- Whole-volume samplers (canisters, bags)
- Concentration samplers (sorbents, SPME)
 - Either case: preservation and analysis in laboratory

Canister samples

- Whole volume
- Grab versus integrated
- EPA Methods TO-14/15
- Benefits:
 - Inert/impermeable
 - Lots of experience
 - Multiple analyses can be done
- Drawbacks
 - Bulky
 - Requires cleaning
 - Can get scratched
 - Sample stability (reactions)



1 – 15 L



400 mL

Tedlar bags

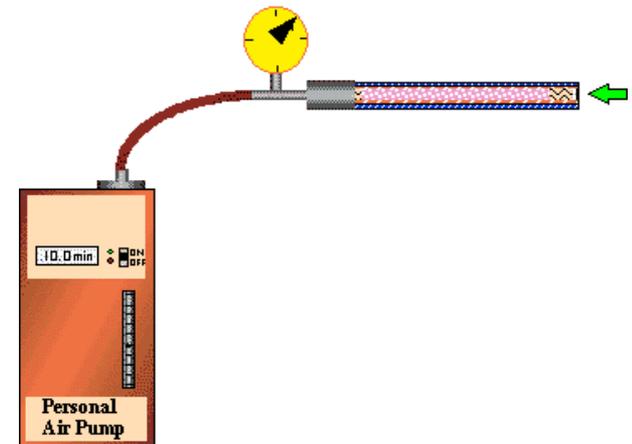
- Whole volume
- Tedlar = polyvinylfluoride
- Pump to collect (unlike canisters)
- Benefits:
 - Inert / impervious (like cans)
 - Repeat samples (like cans)
 - Lighter than cans
 - Lower initial cost than cans
- Disadvantages:
 - Not as reusable as cans
 - Susceptible to tearing
 - Requires cleaning
 - Stability with some compounds



0.5 – 100 L

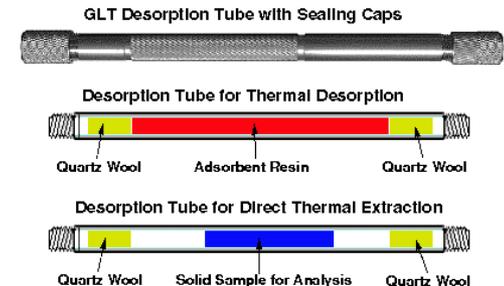
Sorbent sampling

- VOC adsorbs to solid adsorbent
- Passive sampling
 - Similar to ozone badge but w/out reaction
 - Integrated sample over 24 hours, etc.
 - Indoor, personal, outdoor
- Active Sampling
 - Pump air through a packed tube
 - Collect mass over known volume
 - $C = m/V$
 - Short-term vs. integrated
 - More control, but more difficult



Sorbent tubes

- EPA Method TO-17 = TD/GC/MS (important)
- Various sorbents can be used
 - TO-17 page 33
 - Need to match VOC types/ranges with sorbent
- Some issues
 - Method detection limit, precision, accuracy (pg. 28/29)
 - Sample preservation
 - Breakthrough volume
 - Artifact formation (especially via ozone)
 - Sorbent pre-conditioning / breakdown over time
- Use of multi-sorbent beds
- Focus on Tenax-TA

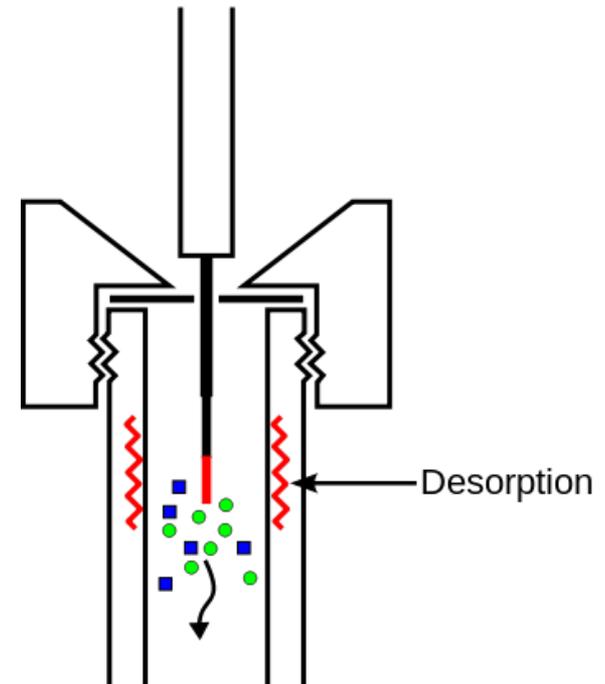


Sorbent: Tenax-TA

- 2,6-diphenylene oxide polymer resin (porous)
- Specific area = 35 m²/g
- Pore size = 200 nm (average)
- Density = 0.25 g/cm³
- Various mesh sizes (e.g., 60/80)
- Low affinity for water (good for high RH)
- Non-polar VOCs ($T_b > 100$ °C); polar ($T_b > 150$ °C)
 - lighter polar – Carbotrap and Carbopack-B common
- Artifacts w/ O₃: benzaldehyde, phenol, acetophenone

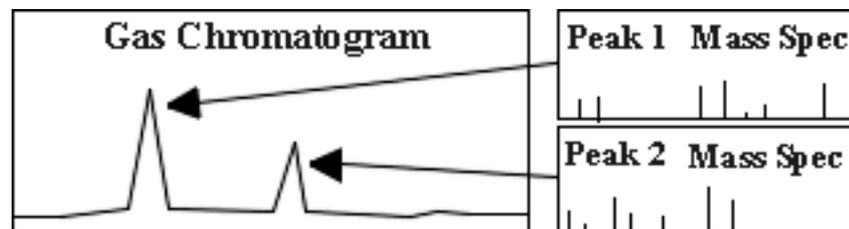
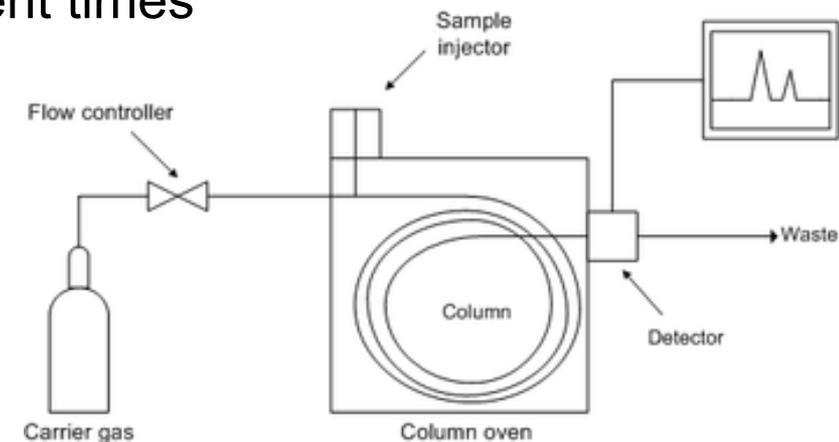
Solid-Phase Micro-Extraction (SPME)

- Uses a fiber coated with an extracting phase:
 - PDMS / DVB / Carboxen
- Benefits
 - Highly concentrating for many indoor VOCs (ppt levels)
 - Can get VVOCs
 - Reusable
 - Relatively low cost
 - Small / light weight
 - Possible use in other media
 - Ease of injection to GC
- Drawbacks
 - Less experience / acceptability
 - Preservation issues
 - Difficulties w/ calibration

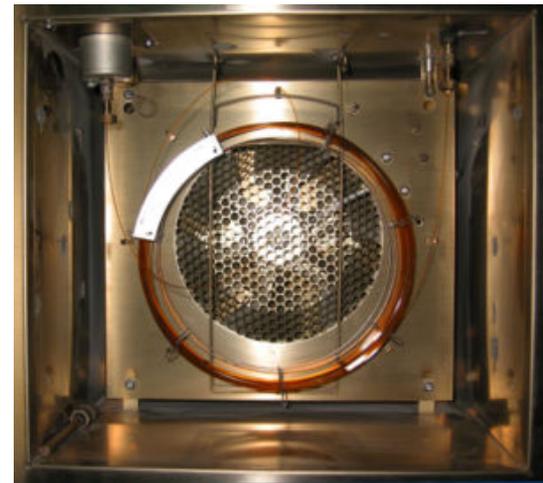
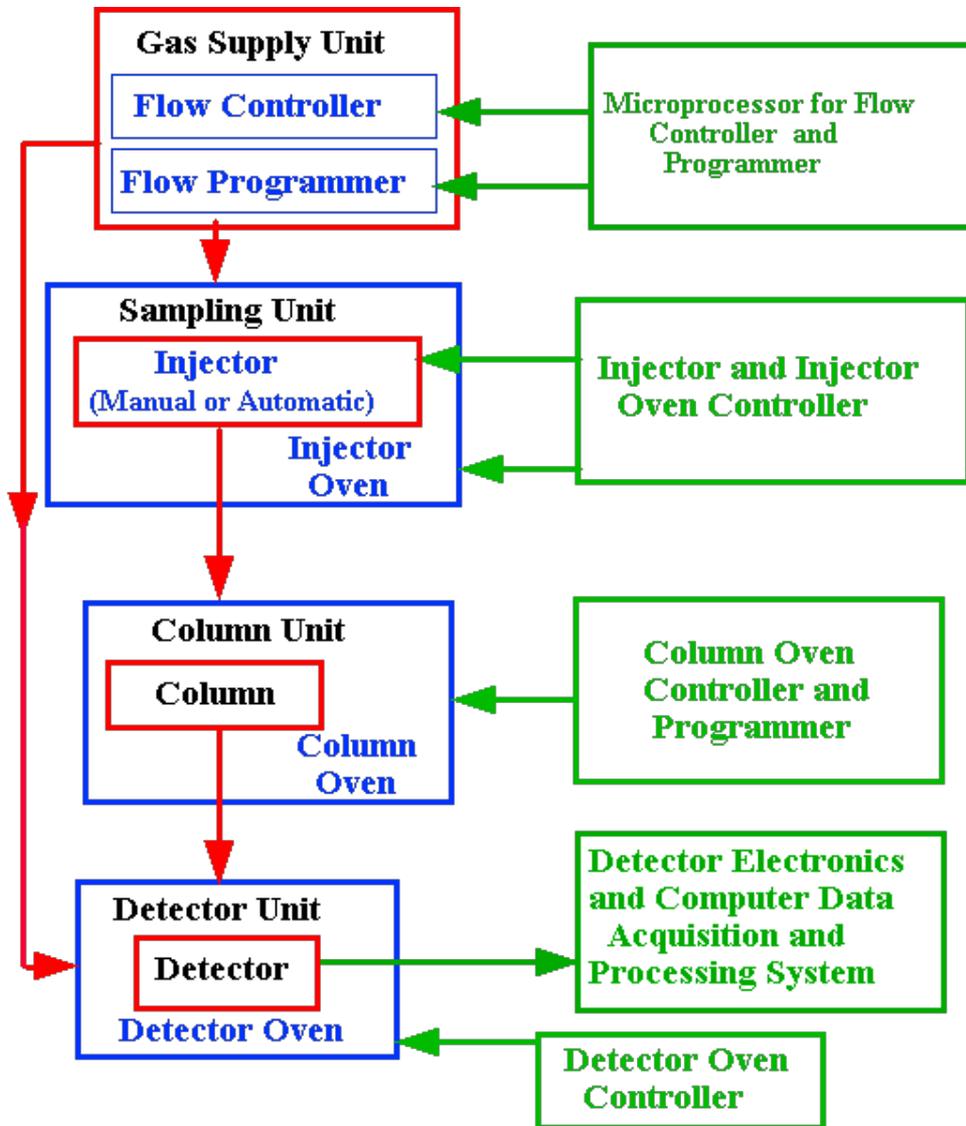


Gas Chromatography (GC)

- GC is used to separate compounds
 - Compounds are vaporized into an inert carrier gas through a capillary column
- Capillary column
 - Stationary microscopic layer of liquid or polymer on inert solid support inside a piece of glass or metal tubing
 - Causes compound to elute at different times
 - Retention time
- Thermal program of GC oven
- Temporal passage to a detector
 - Analyze “peaks”
 - Analyze molecular fragments (MS)



Gas Chromatography (GC)



GC issues

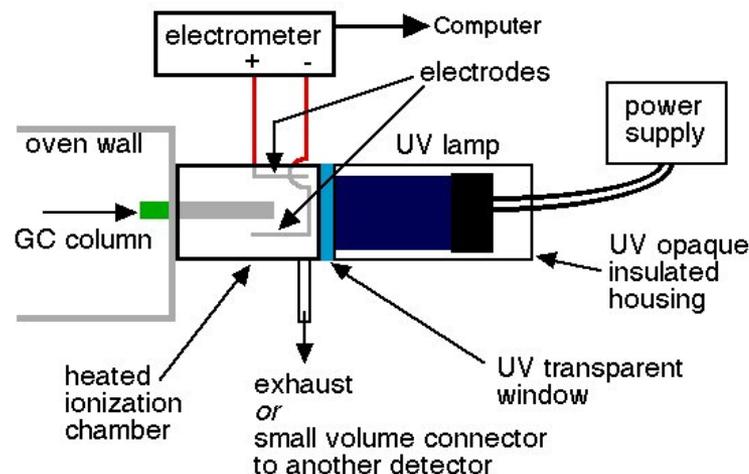
- Type of injection?
- Need to cryo focus for low molecular weight volatiles?
- Type of column?
- Type of detector?
 - If MS, model of detection
- Temperature programs
- Instrument calibration / response

Detectors

- Flame ionization detector (FID)
 - Photoionization detector (PID)
 - Electron capture detector (ECD)
- } Non-specific or speciated (w/ GC)
-
- Mass spectrometer (MS)
- } w/ speciated (w/ GC)
-
- These are primary detectors for VOCs in indoor air
 - Specific uses vary considerably

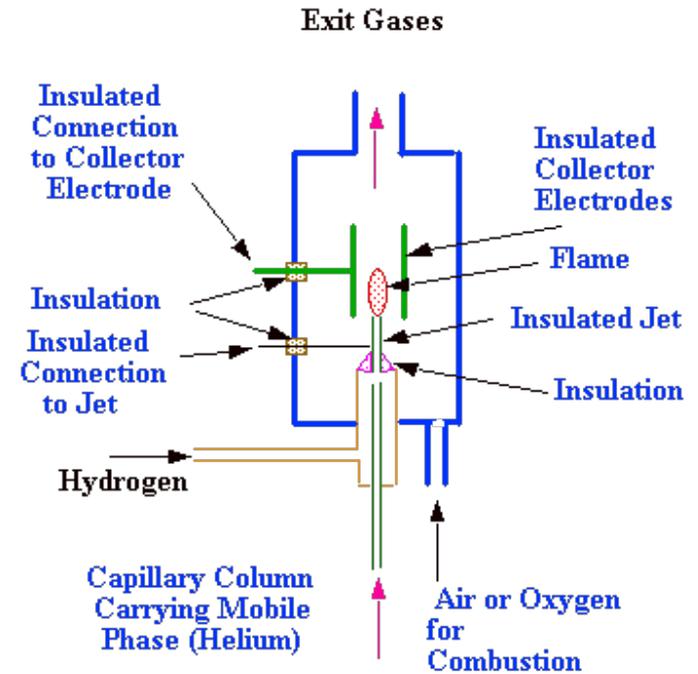
Photoionization Detectors (PID)

- UV light ionizes VOCs --- $R + h\nu \rightarrow R^+ + e^-$
- Collected by electrodes = current
- VOCs with different ionization potential
- Benefits
 - Simple to use
 - Sample non-destructive (relatively)
- Drawbacks
 - No identification/speciation
 - Highly variable responses
 - Not all VOCs detected
 - Lamp burnout / contamination



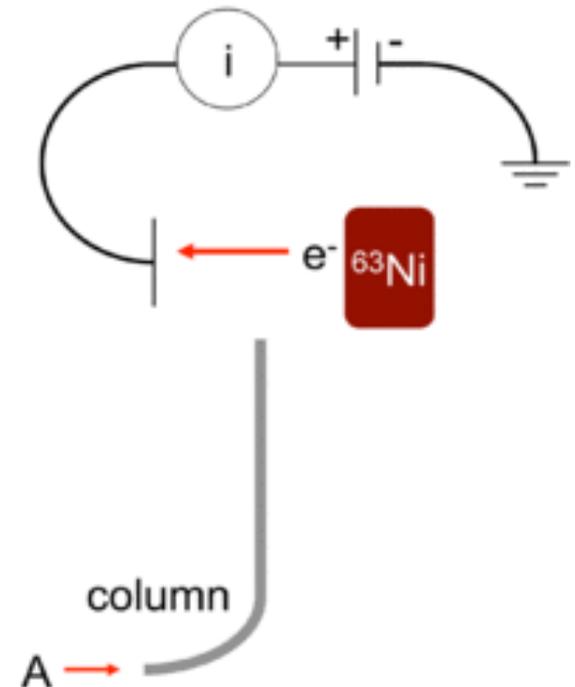
Flame Ionization Detectors (FID)

- Relatively simple system
- Hydrogen flame → ions formed
 - Ions migrate to plate, generate a current
 - Hydrocarbons have molar response proportional to the number of carbon atoms in their molecule
- Detection – typical to pg/s
- Benefits
 - Rugged, low cost, workhorse
 - Linear response over wide range
 - Insensitive to H₂O, CO₂, SO₂, CO, NO_x
- Drawbacks
 - No identification
 - Lower response if not simple HC
 - Destructive testing



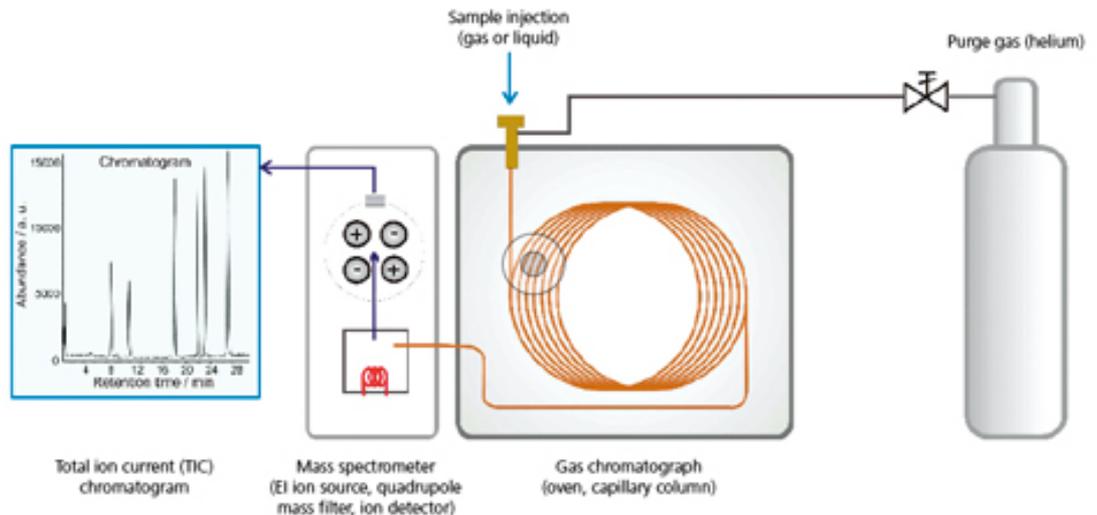
Electron Capture Detectors (ECD)

- Low energy Beta emitter = ^{63}Ni in make-up gas (Nitrogen)
- e^- attracted to positively charged electrode (anode)
- Molecules in sample absorb e^- and reduce current
 - effective: halogens (e.g., SF_6), nitrogen-containing compounds
- Benefits
 - 10-1000 times more sensitive than FID
 - femtogram/s ----- ppt levels
- Drawbacks
 - More limited linear range than FID
 - Radiological safety requirements
 - O_2 contamination issues
 - Response strong function of T, P, flow rate



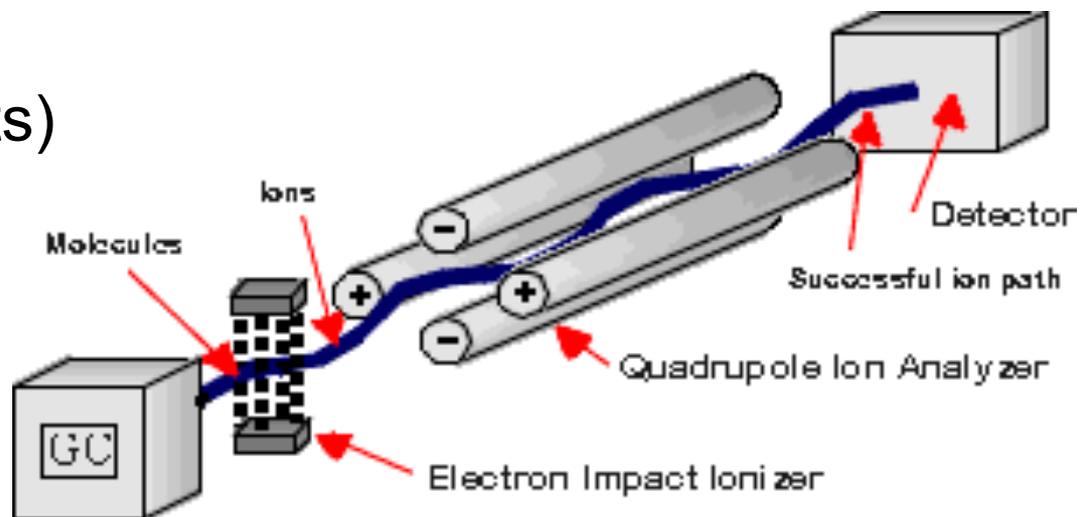
Mass Spectrometer (MS)

- Bombard molecules w/ intense electron source (ionization)
 - Generates positive ion fragments
- Ions accelerate to have same kinetic energy, then deflect in a magnetic field, where deflection is a function of molecular weight
- Use fragment fingerprint to identify molecule
- Quantify amount of fragments to determine mass
- Most common MS = quadrupole
- Benefits
 - “Gold standard”
 - Amount AND identific
- Drawbacks
 - Cost
 - Complexity
 - Maintenance

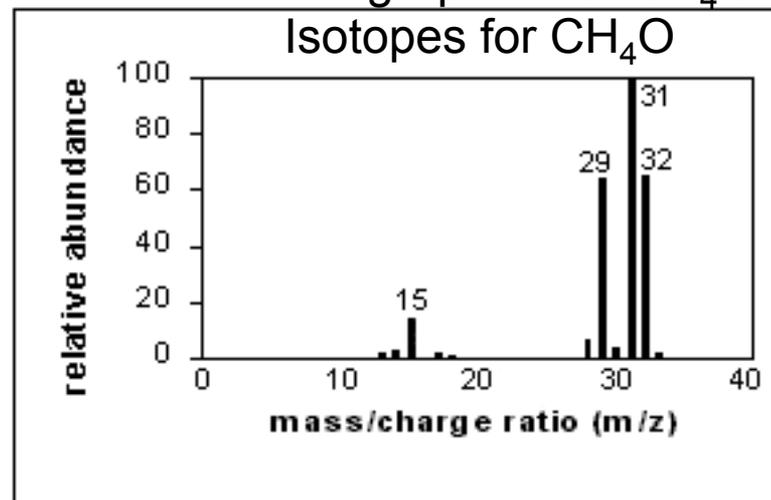


Quadrupole MS

- Electron source
- Four rods (electromagnets)
 - Applied Voltage
 - DC/AC components
 - Voltages = $f_n(\text{time})$
 - Affects trajectory
 - Selective M/Z to detector
 - m/z = mass-to-charge ratio
 - Ionization makes $z = 1$
- Cycles different M/Z
- Yields mass spectrum
- Always same for a molecule
- System in vacuum



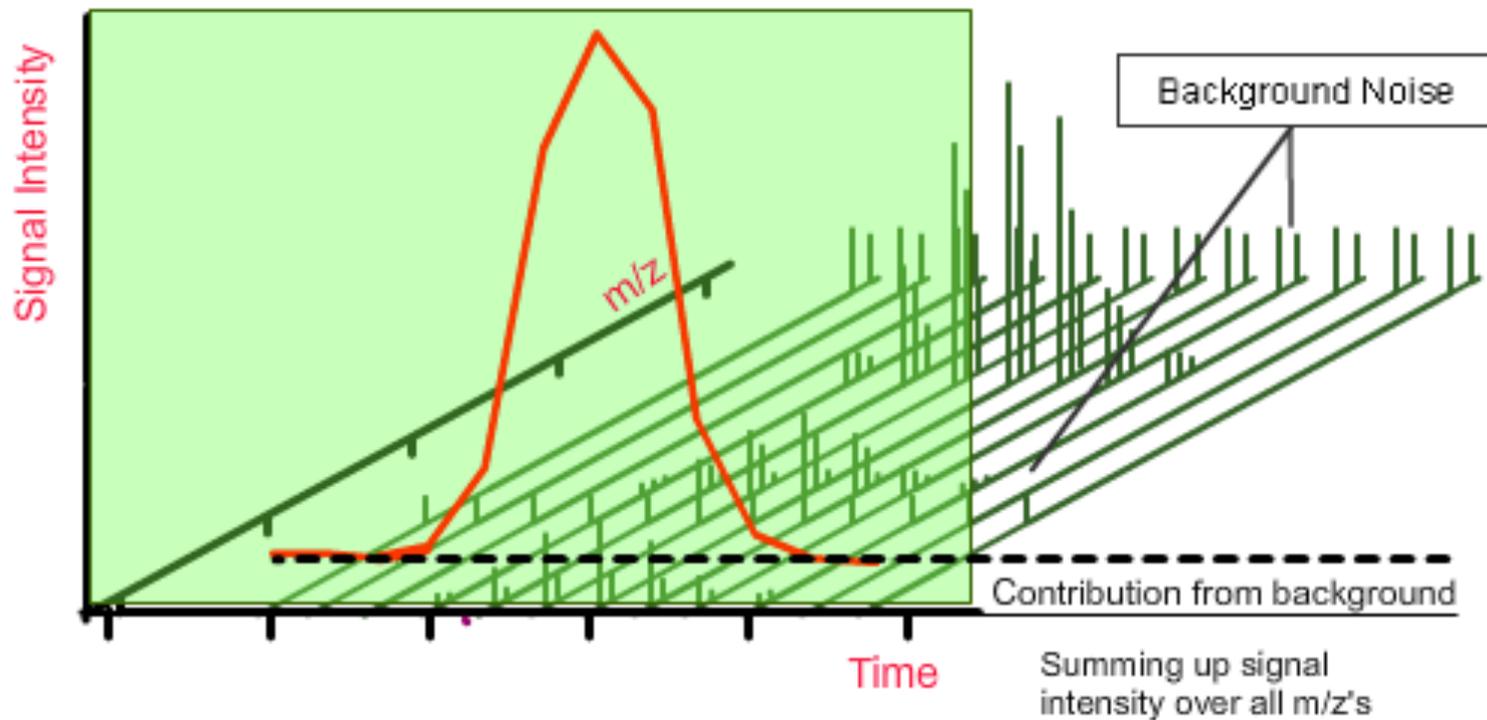
“Fingerprint” for CH_4O :
Isotopes for CH_4O



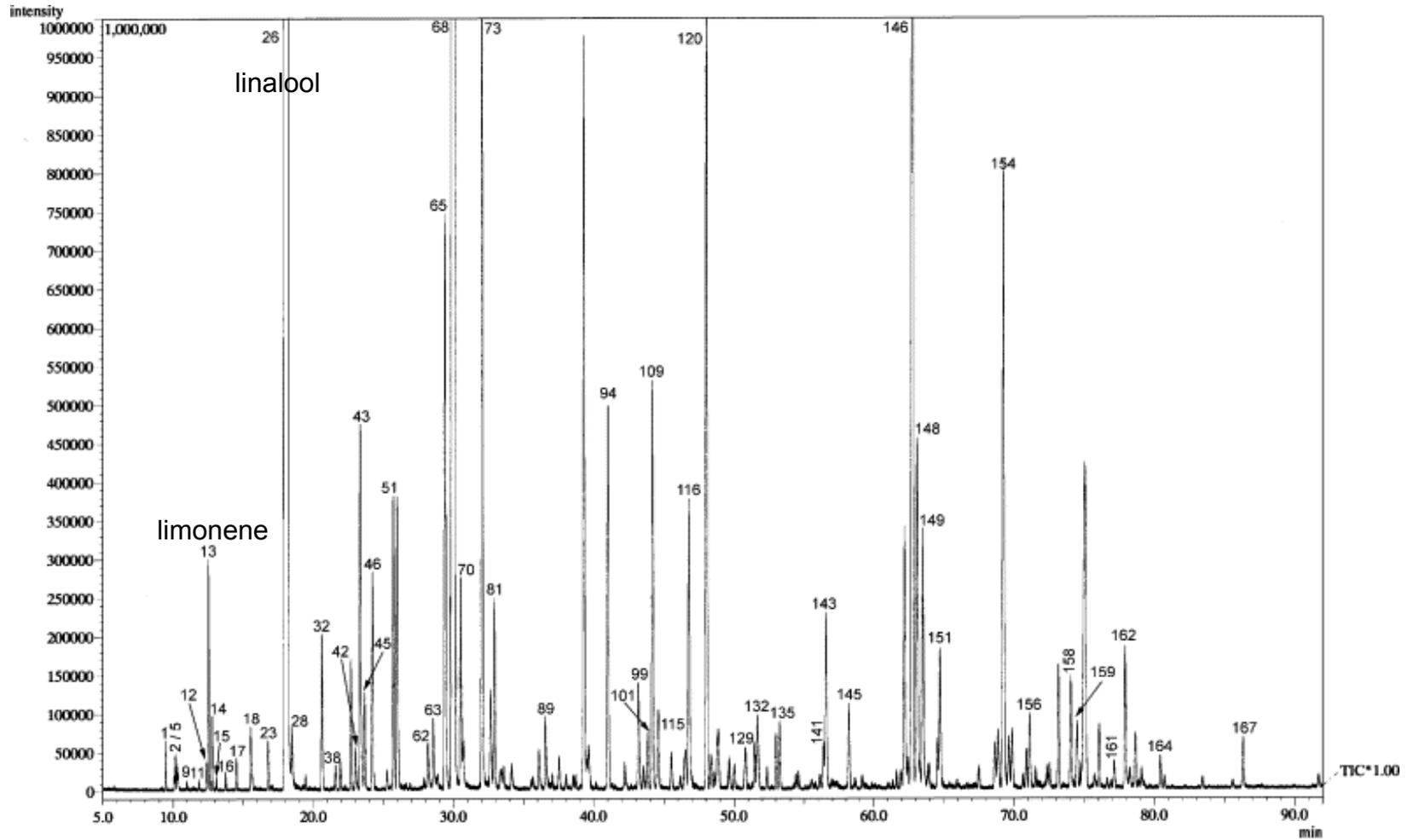
ions	m/z
CH_3OH^+	32
$\text{H}_2\text{C}=\text{OH}^+$	31
$\text{HC}\equiv\text{O}^+$	29
H_3C^+	15

Total Ion Chromatogram (TIC)

Sum up intensities of all mass spectral peaks belonging to the same scan

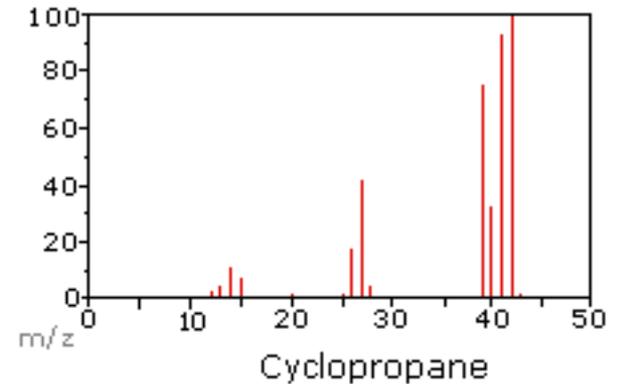
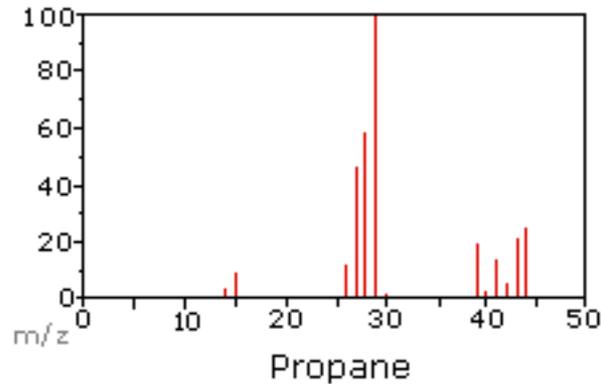
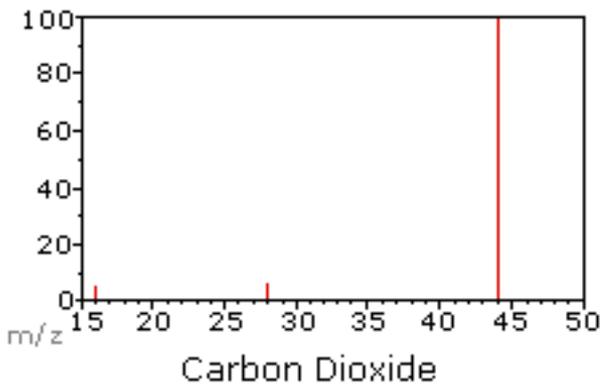
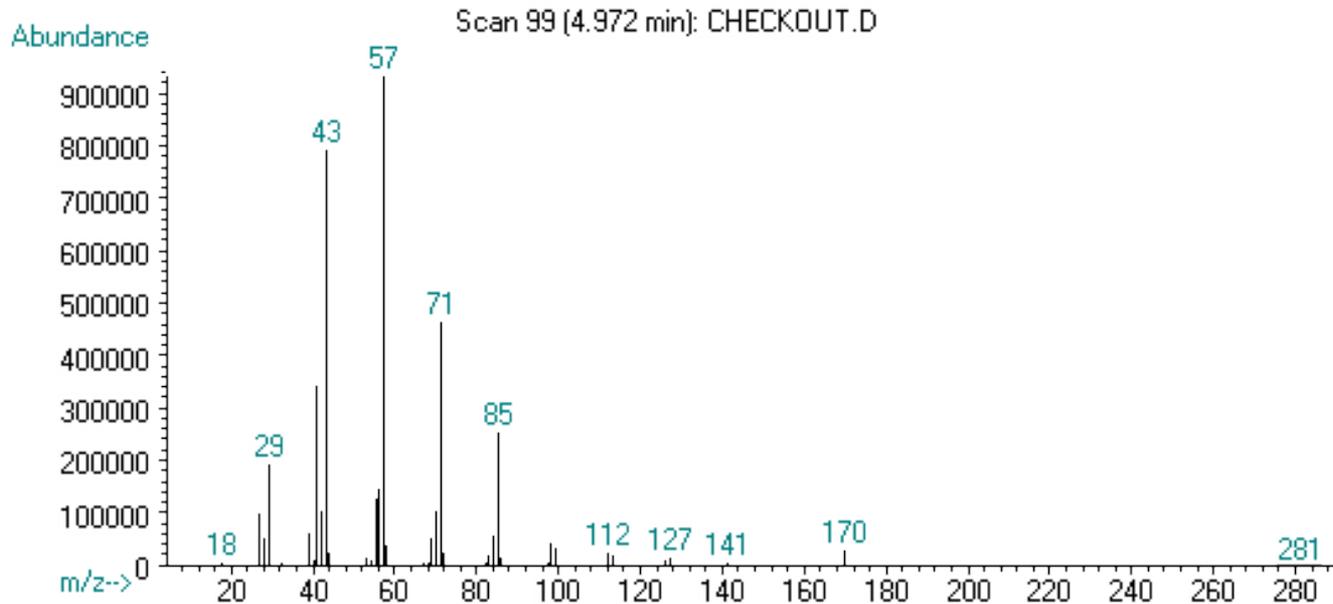


Total Ion Chromatogram (TIC)



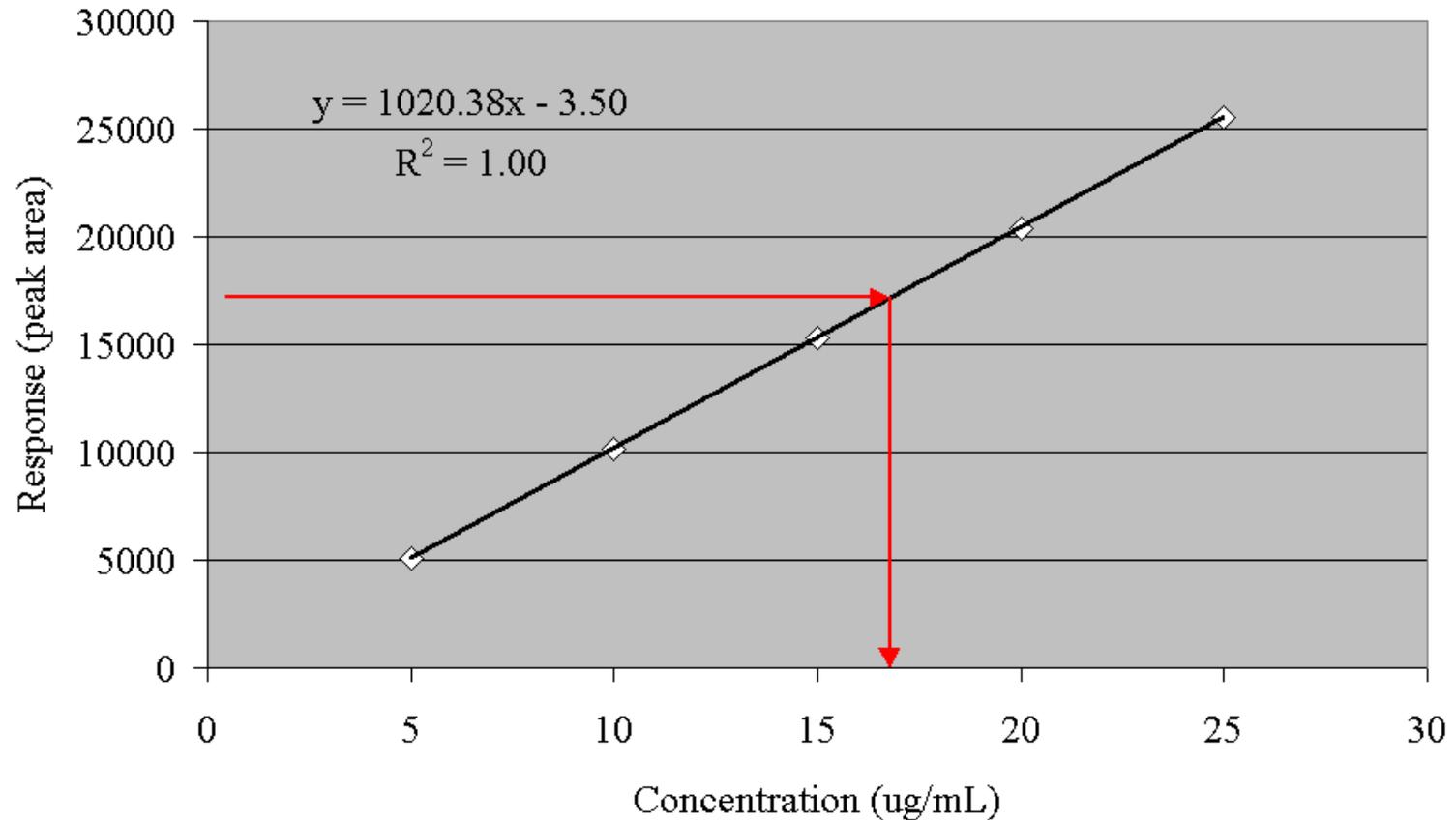
Mass spectrum

Example mass spectrum (fingerprint)



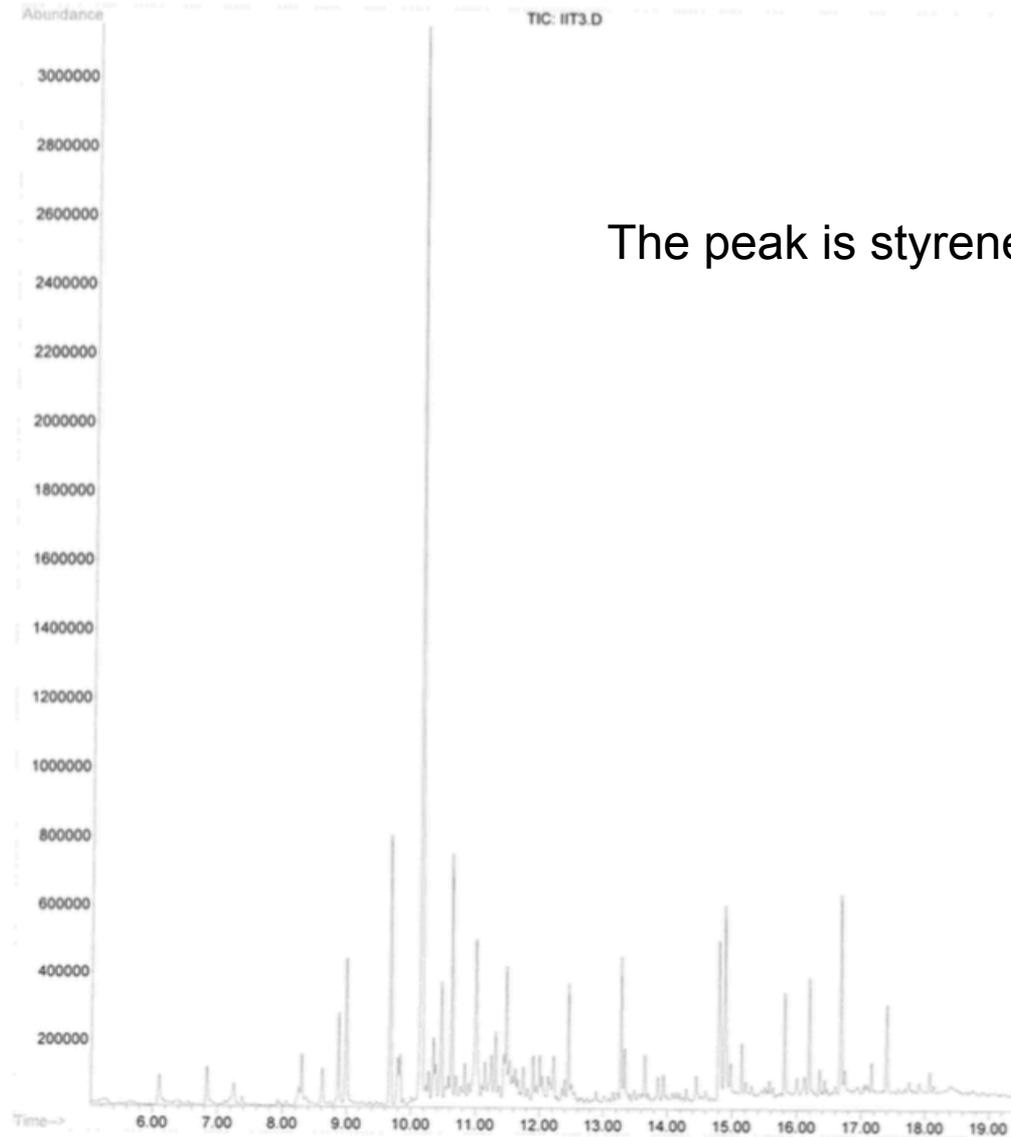
Calibration curves

Calibration Curve for Compound X



$$\text{Response Factor} = \frac{\text{Peak Area}}{\text{Calibration Concentration}}$$

Real VOC data w/ library compound search



Summary of VOC measurements

- VOCs important in indoor environments
- Many types of VOCs
 - Different properties
 - Different effects
 - Different sample collection and analysis protocols
- Sampling and analysis protocols NOT TRIVIAL
 - Many types of collection methods
 - Many types of analysis detectors and methods
 - A lot of issues involved w/ sample/analysis decisions
 - A lot can go wrong (difficult business)
 - Cumbersome and costly, but very important