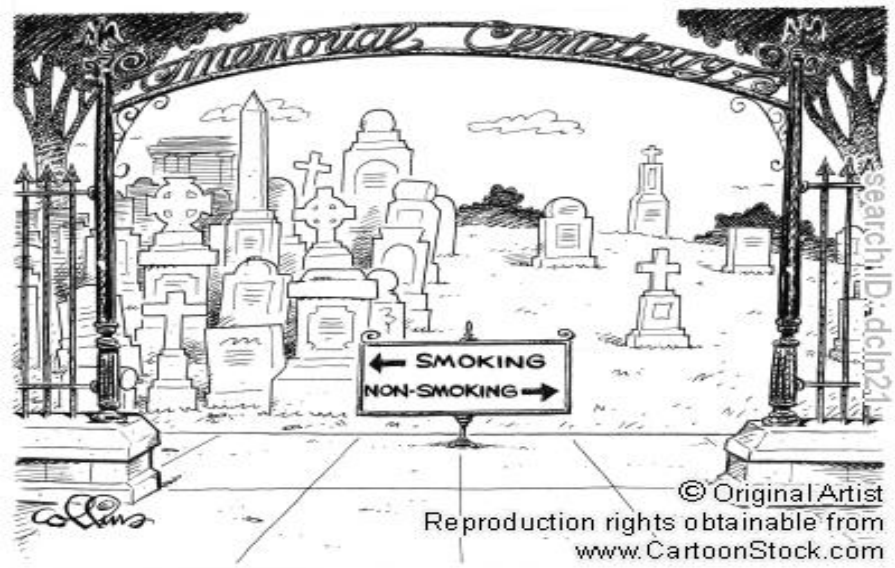
3rd Hand Smoking: Heterogeneous Oxidation of Nicotine and Secondary Aerosol Formation in the Indoor Environment

Lauren Petrick and Yael Dubowski



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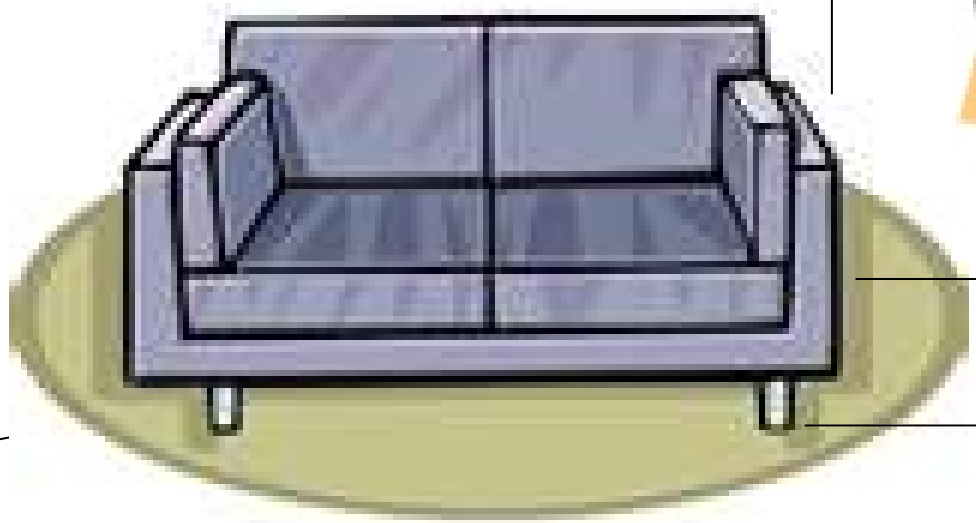
Indoor pollutants dynamics

VOC off-gassing, cleaning products, pesticides, cigarettes

O_3, NO_x, particles



Chemical reactions

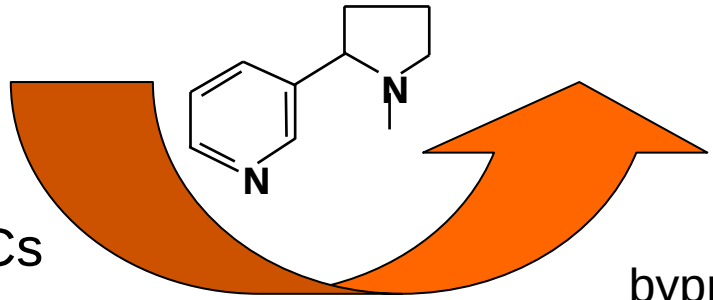
Tobacco smoke in the indoor environment

So, is O_3-cleaning a good solution?

Volatile organic compounds (VOC) ⟶

Particulate matter (PM) - - - - ⇢

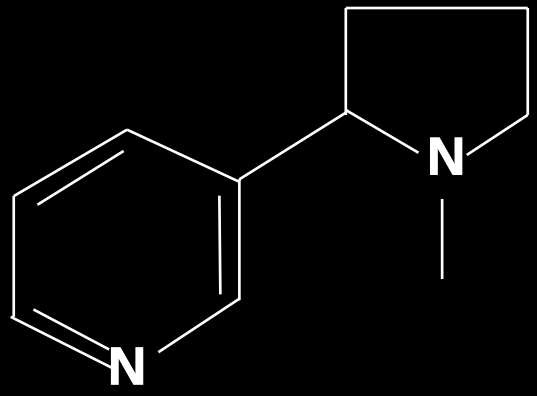
VOC ⟶ + O_3 ⟶ 2nd VOCs, PM



SVOCs

re-emitted SVOCs and byproducts of indoor chemistry

INDOOR SURFACES



RH

AER

O_3

Building Parameters

Nicotine Dynamics

Surface Parameters

physical

chemical

?

1) What material will nicotine preferably sorb to?

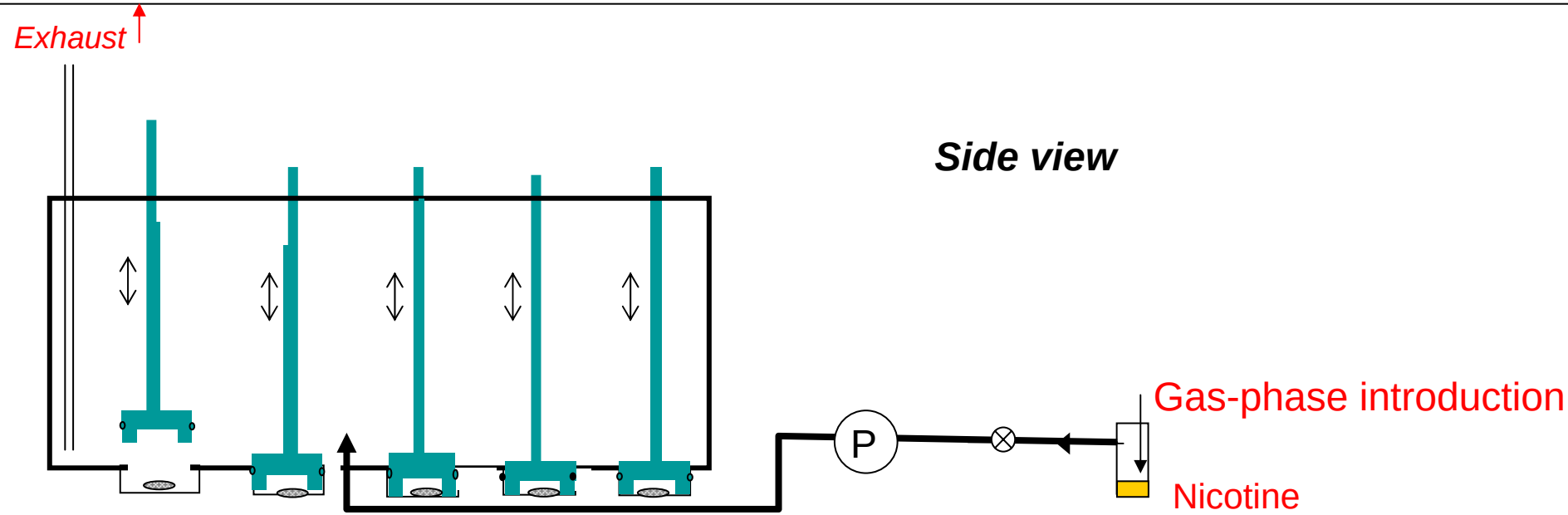
2) what are the effects of AER, RH, and substrate type on surface nicotine loss ?

3) Effects of RH?

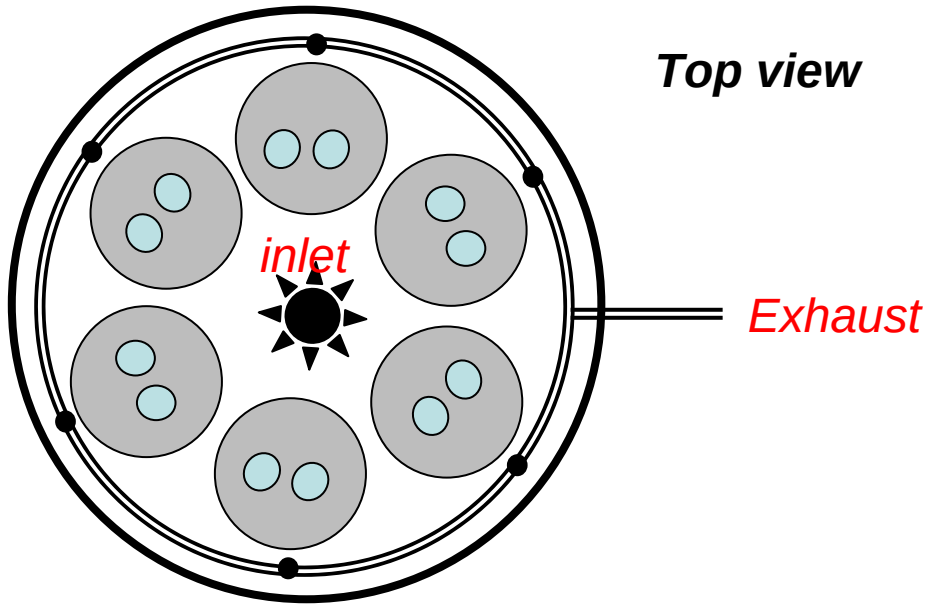
4) Product identification

5) SOA formation

Flow-through sorption setting



Glass
Polyester
Wood
Cotton
Nylon
Wallboard paper



Nicotine sorption

All cellulose materials

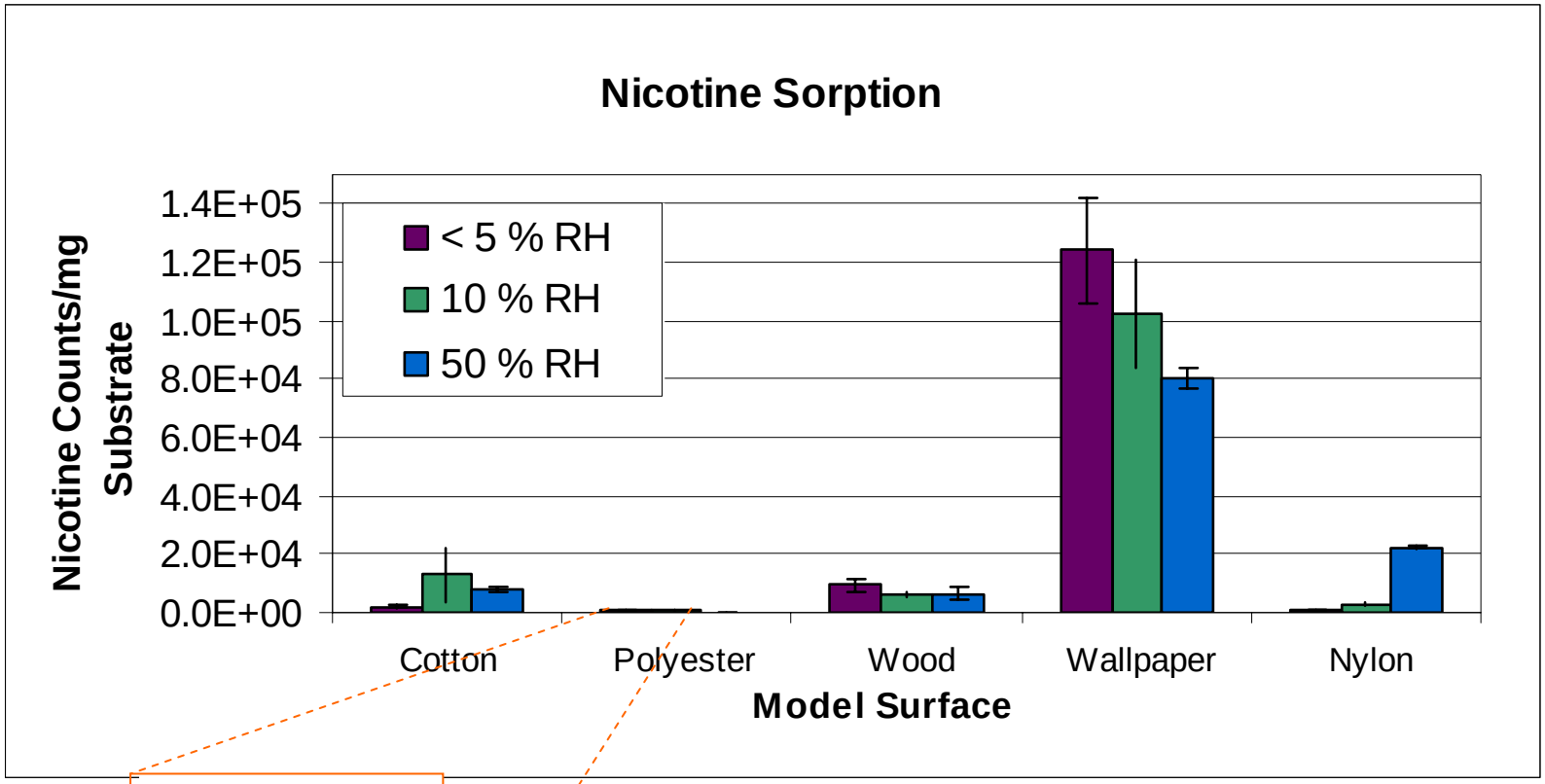
- **Wallboard paper**
- **Wood**
- **Cotton**
- **Nylon / Polyester / Glass**

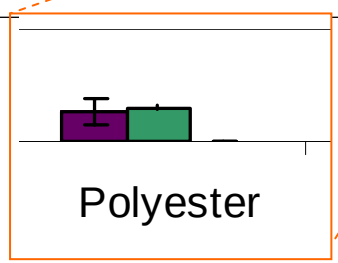
Sorbed Nicotine

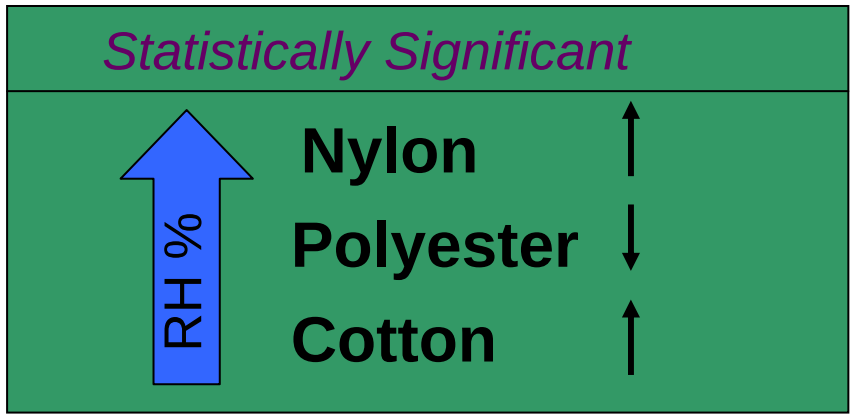
- Although nylon and polyester have only 75% and 25% less surface area than cotton nicotine level on these surface was much lower.

→ Surface morphology is not the only factor affecting sorption.

RH Effect

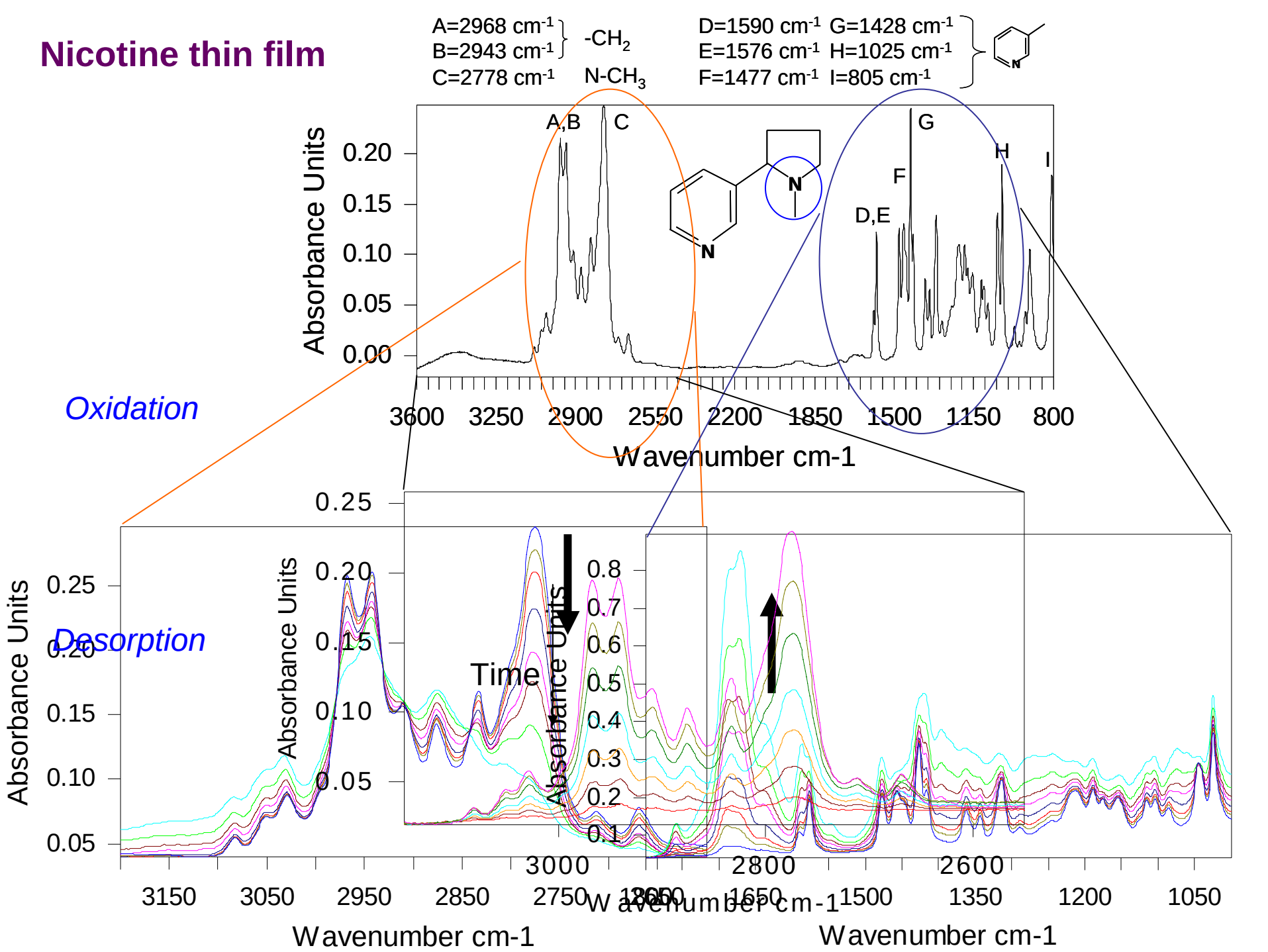

Nicotine Sorption
Nicotine Counts/mg Substrate
1.4E+05
1.2E+05
1.0E+05
8.0E+04
6.0E+04
4.0E+04
2.0E+04
0.0E+00
< 5 % RH
10 % RH
50 % RH
Cotton
Polyester
Wood
Wallpaper
Nylon
Model Surface


Polyester


Statistically Significant
RH %
Nylon
Polyester
Cotton


RH
control
Ozone
generation
Outlet
Mixing
bulb
Inlet

Nicotine thin film



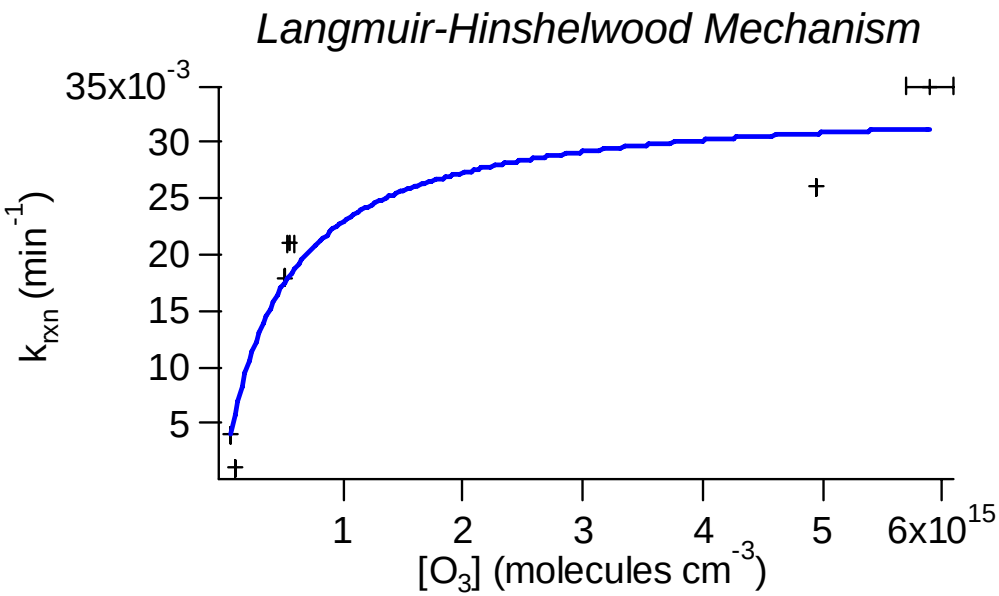
kinetics

$k_{obs} = k_d + k_{rxn}$

Film type	*Relative Humidity**	*AER (h^{-1})*	*Rate (min^{-1})*
Desorption (k_d)			
Cellulose	High	15	0.060 ± 0.007
Cellulose	Low	15	0.050 ± 0.004
Cellulose	Low	3	0.031 ±0.002
No cellulose	Low	15	0.118 ± 0.013
Observed Oxidation** (k_{obs})			
Cellulose	High	15	0.089 ± 0.006
Cellulose	Low	15	0.085 ± 0.014
Reaction (k_r)			
Cellulose	High	15	0.029 ± 0.009
Cellulose	Low	15	0.035 ± 0.015

* High: > 75% RH; Low: < 10% RH ** $[O_3] = 6 \pm 0.3 \times 10^{15}$ molecules/cm^3

Off-line Experiments: cotton doped with nicotine

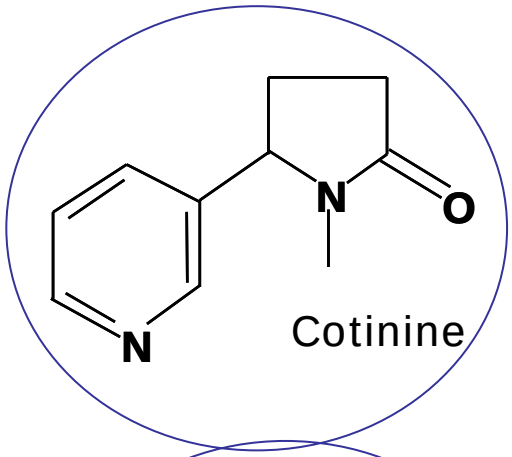


$$k_1 = \frac{k_s[S]K_{O3}[O_3]_{gas}}{1 + K_{O3}[O_3]_{gas}}$$

$k_1^* = 7.4 \times 10^{-5}$ min^{-1} at $[O_3]_g$ = 40ppb

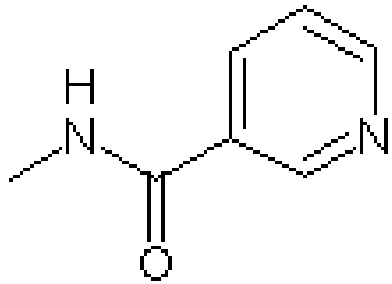
→ $t_{1/2}$ ~ 6 days

Identified surface oxidation products



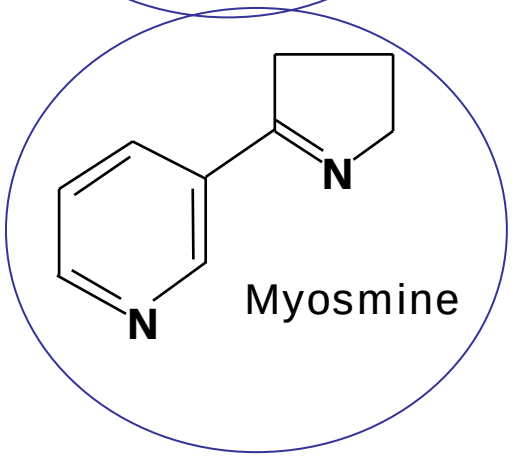
Cotinine

θ=9% (cellulose)
θ= 11% (cotton)

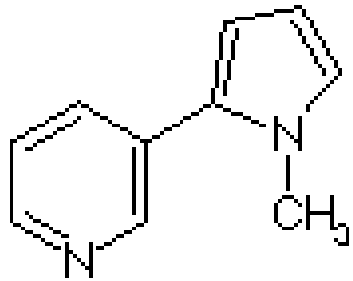


N-methylnicotinamide

θ=3% (cellulose)
θ= 6% (cotton)



Myosmine

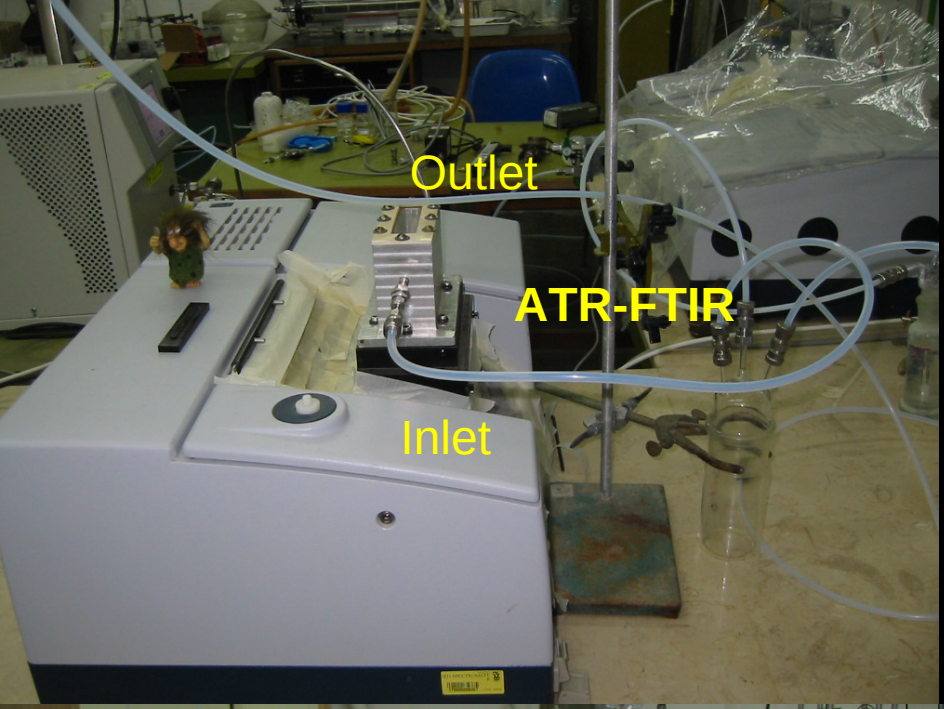


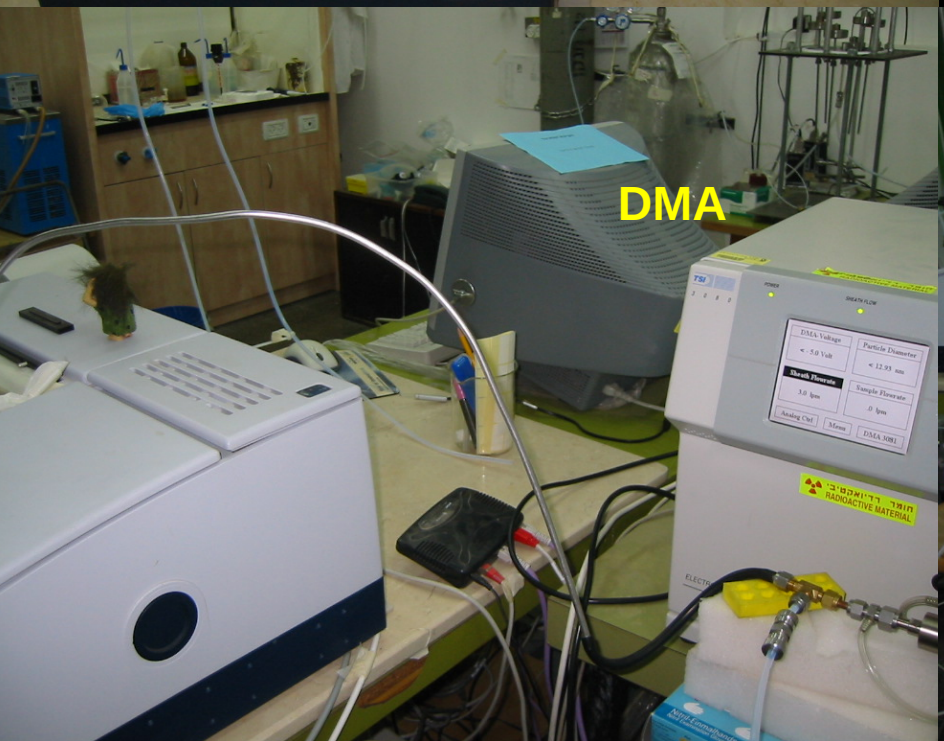
Nicotyrine

→ *Mutagen/carcinogen/teratogen potential*

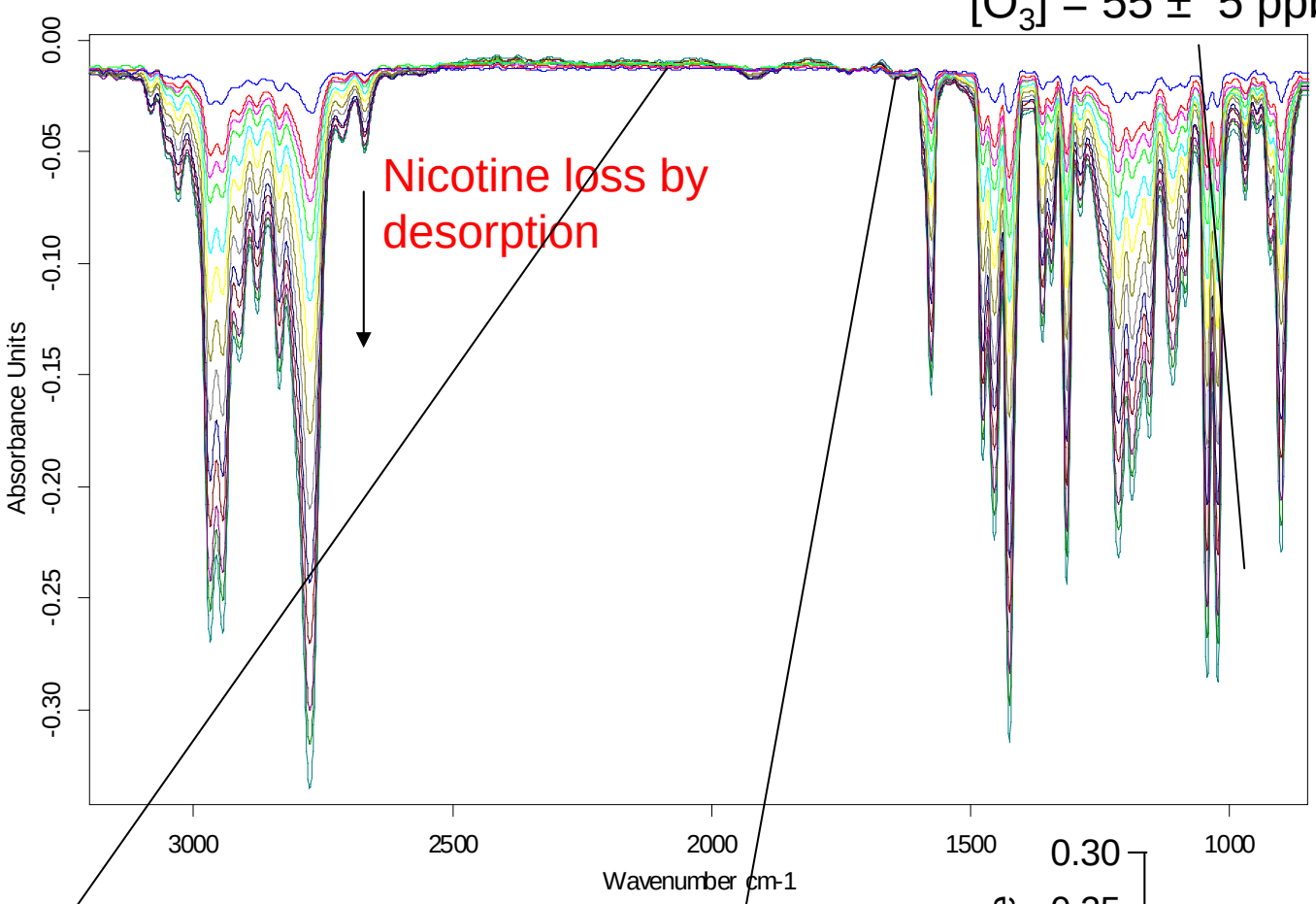
Tandem ATR-FTIR-SMPS

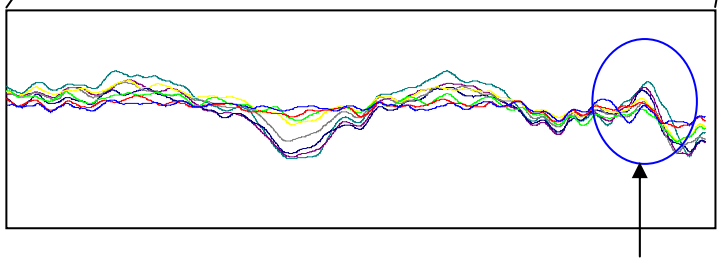
- Surface kinetics and SOA formation

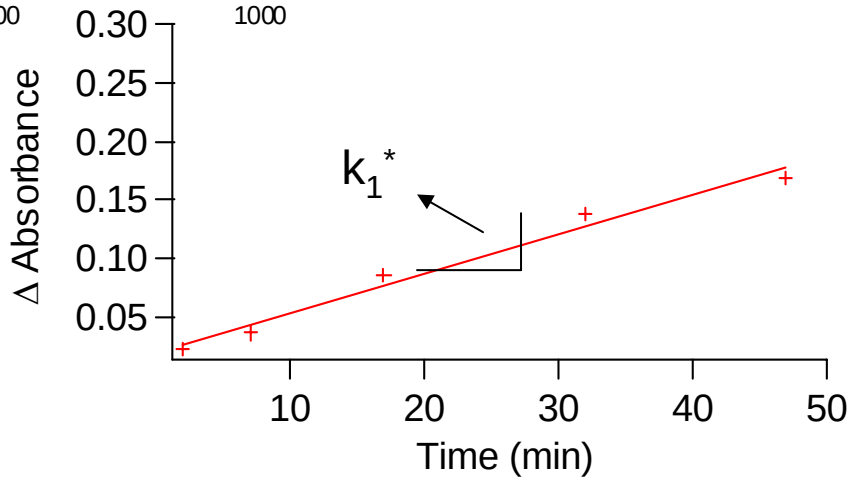




ATR-FTIR







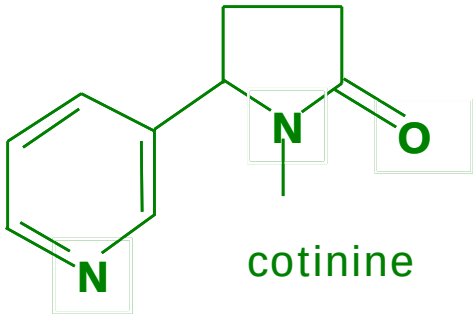
RH < 5%

$k_1^* = 0.0026 \pm 0.0007\ min^{-1}$

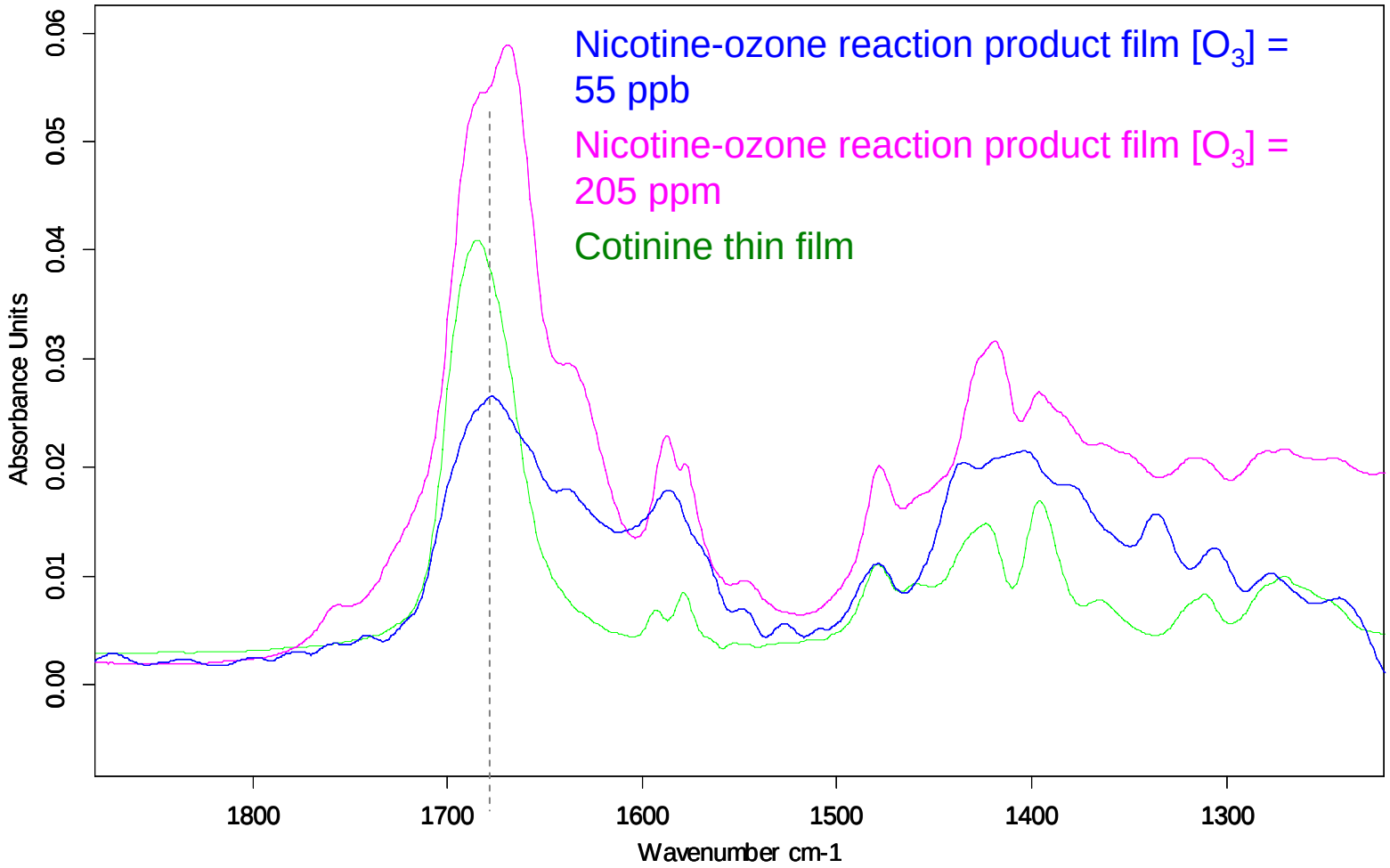
RH ~ 40%

$k_1^* = 0.0010 \pm 0.0002\ min^{-1}$

Nicotine-ozone surface product film

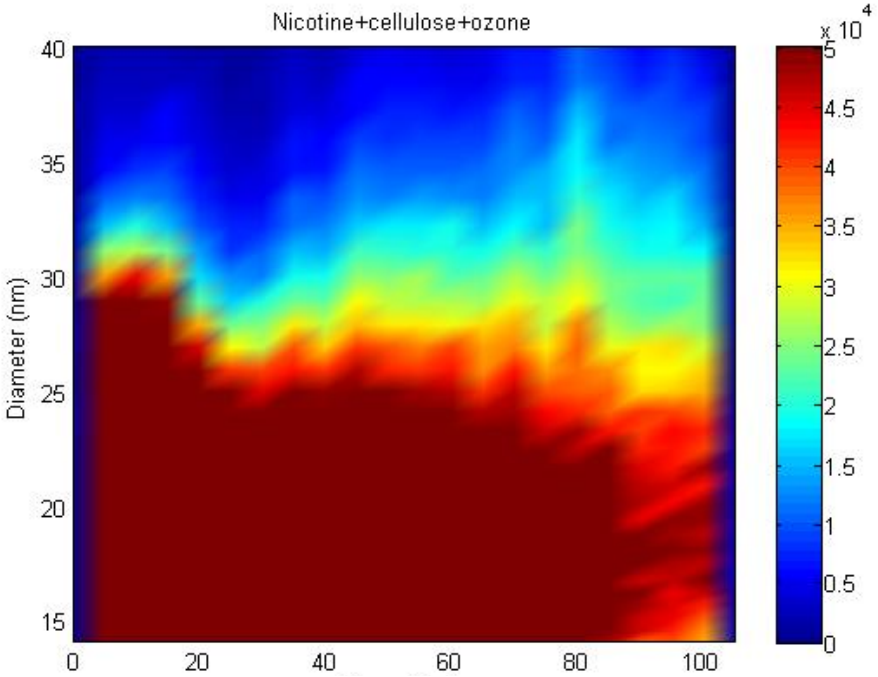


cotinine

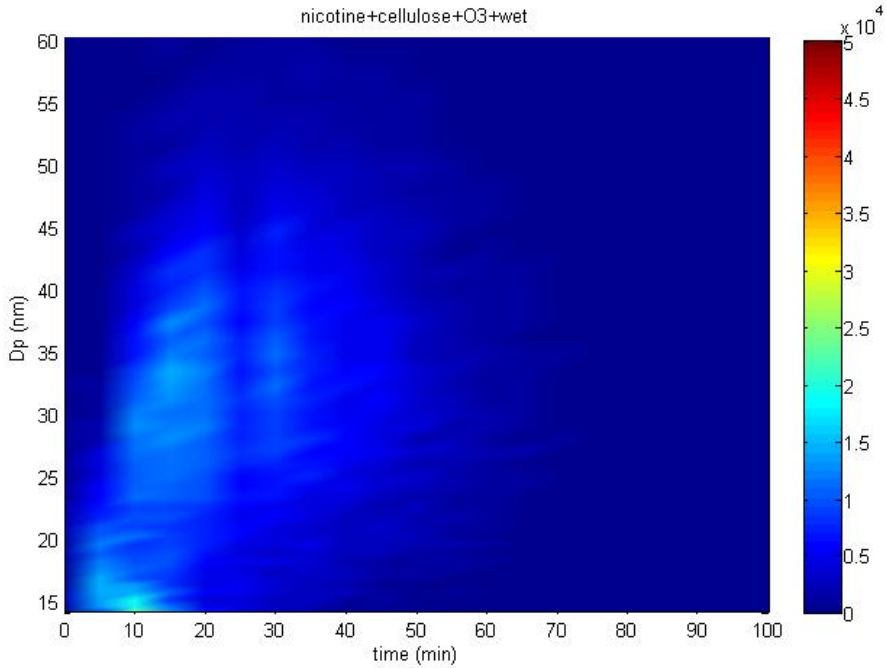


Nicotine sorbed to cellulose

SMPS



Dry (<5 % RH) :



Ambient (~40 % RH) :

 # Total Particles

Dry >> Ambient RH

→ *Less reaction*

Conclusions:

1) Sorption, desorption, parameter effects:

- ❖Nicotine preferably sorbs to high-polarity materials.
- ❖Nicotine sorption is affected by RH, facilitating or hindering sorption depending on polarity of material
- ❖Nicotine desorption and oxidation rates are affected by RH, AER, and substrate

2) Rate constants at $[O_3]$ = 40 ppb:

Method	**k_1* (min^{-1})**	**~$t_{1/2}$**	**RH Effect**
L-H mech.	7.4×10^{-5}	6d	Slightly hindered
Linear ext.	2.0×10^{-3}	12h	$k_1^* = 8.0 \times 10^{-4}$
Gas phase†	5.4×10^{-4}	1d	No meas reaction

† Destaillats et al. ES&T 2006

→ Ozonation of nicotine sorbed to cotton had similar kinetics at high $[O_3]$, but not measurable at $[O_3]$ = 55 ppb

3) SOA formation at [O_3] = 55 ppb:

- ❖ SOA yield

  Dry~30%.

  Ambient RH ~ 5%

- ❖ No SOA detected from reaction of nicotine sorbed to cotton

- ❖ Homogenous or heterogeneous reaction?

  1) AER >> $k_1^*{}_{(gas)}$ (Tuazon, et al. 1994)

  2) Back of the envelope calculations:

  2×10^{-5} ng cm^{-3} of gas phase nicotine reacted

  $24\text{-}7 \times 10^{-4}$ ng cm^{-3} of total particle mass formed

→heterogeneous

4) *So, is O_3-cleaning a good solution?*

Formation of SOA and oxidation products:

Myosmine→ confirmed mutagenic effects

Cotinine→ potenital mutagenicity and teratogenicity

Thank You

For your attention

And to Hugo Destaillats, Irena Zouev, Sara Sabach and Hodayah Hadar-Abuhatzira for their help

Questions?

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