

EUROCHAMP final meeting  
May 14-15<sup>th</sup>, 2009

**In-cloud processing of secondary  
organic aerosols**  
*Preliminary study*

**Liu Y., Temime-Roussel B., Quivet E., Marchand N., Monod A.**

LCP, CNRS-Université de Provence, Marseilles, France

**DeCarlo P., Tritscher T., Praplan A., Dommen J., Baltensperger U.**

PSI-LAC, Villigen, SWITZERLAND



# Tropospheric Clouds



- ☞ **Surface cover : about 60% of the Earth's surface**
- ☞ **Lower troposphere : first 4-6 km altitude**
- ☞ **A small fraction (about 10%) of clouds precipitate (rain)**
- ☞ **Significantly influenced by surface emissions**

**Cloud water droplets** → **Chemical photoreactors**

Monod *et al.*, 2005

Herrmann *et al.*, 2005

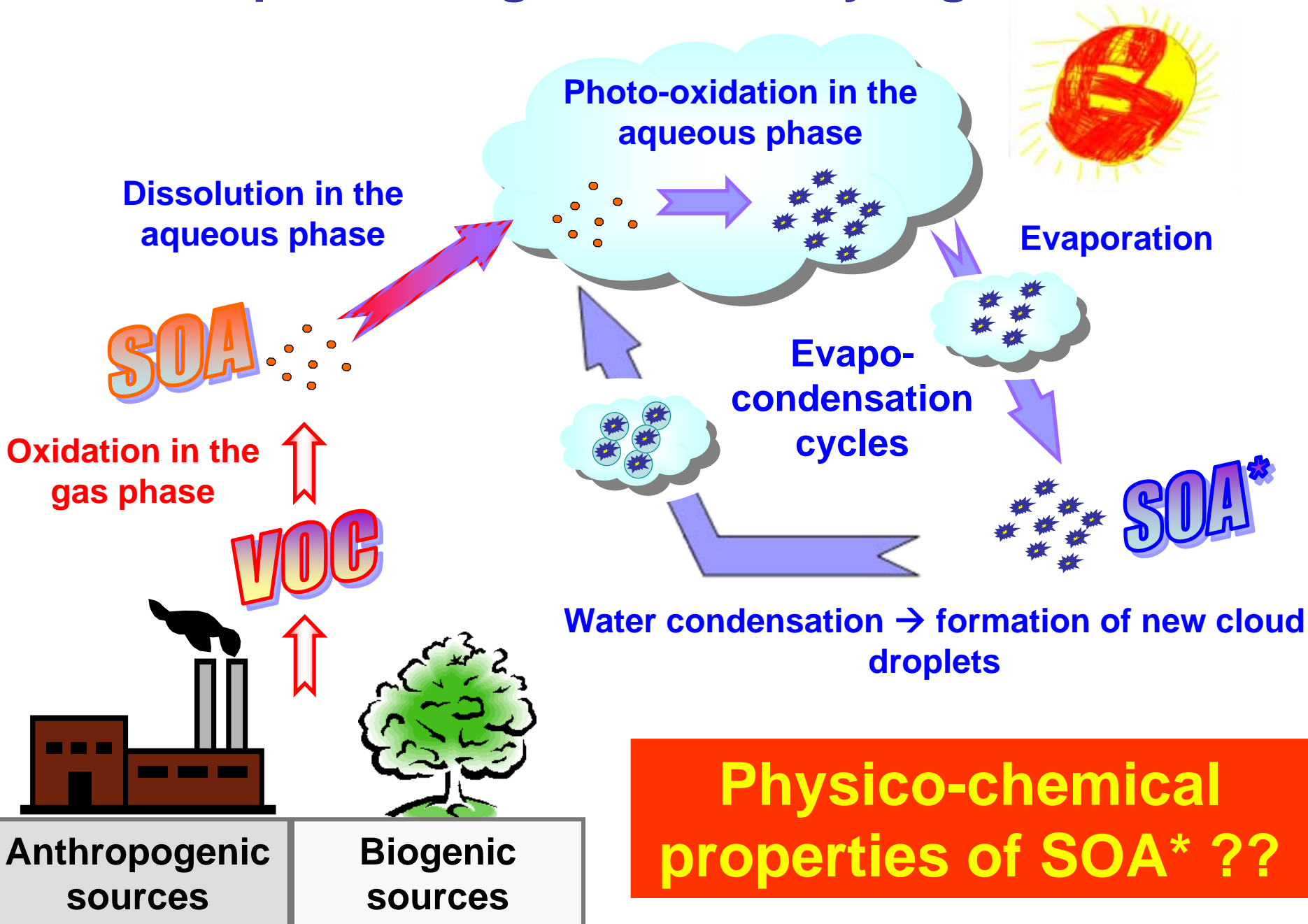
Altieri *et al.*, 2007

Carlton *et al.*, 2007

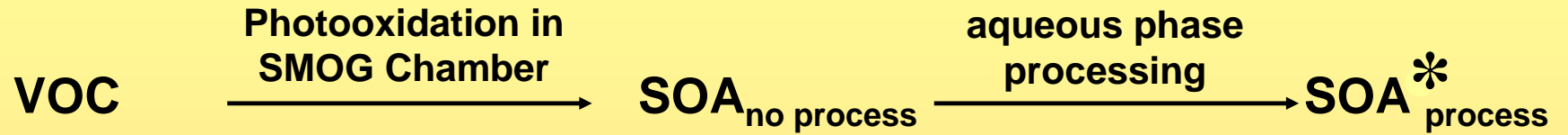
Liu *et al.*, 2009

El Haddad *et al.*, 2009...

# In-cloud processing of secondary organic aerosols



# Methodology

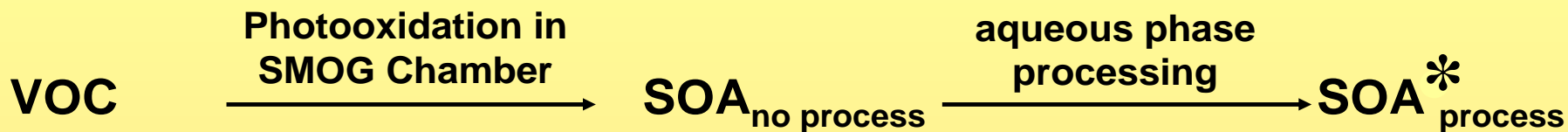


Isoprene

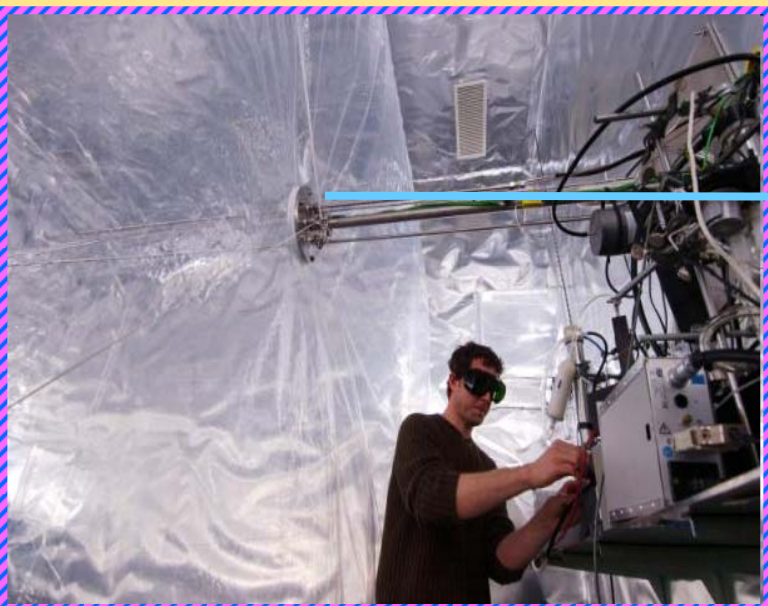
$\alpha$ -pinene

1,3,5-TMB

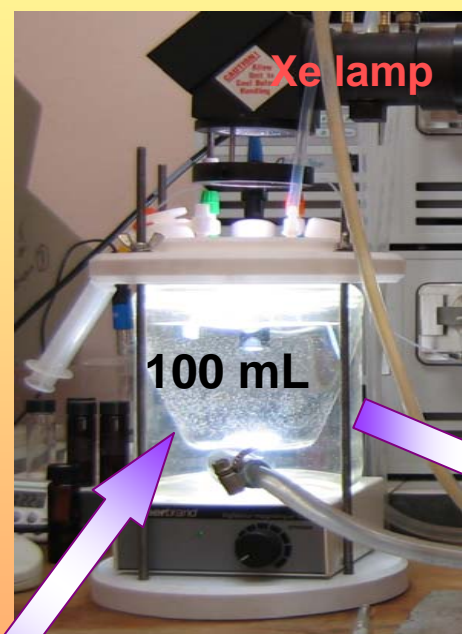
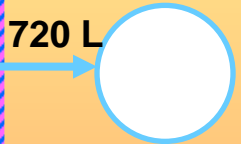
# Experimental protocol: general overview



Isoprene  
 $\alpha$ -pinene  
1,3,5-TMB



PSI SMOG chamber



Aqueous phase photoreactor

Nebulization

# Experimental protocol: general overview

VOC

Isoprene

$\alpha$ -pinene

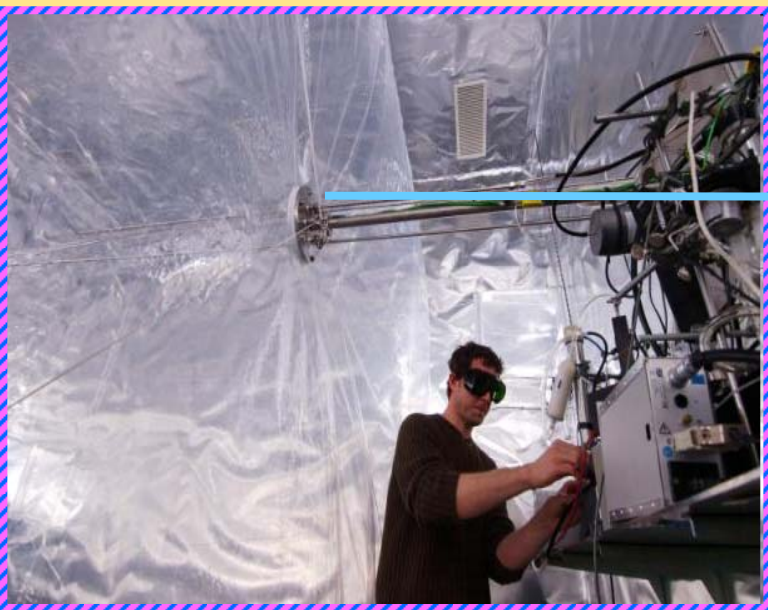
1,3,5-TMB

Photooxidation in  
SMOG Chamber

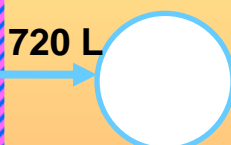
SOA<sub>no process</sub>

aqueous phase  
processing

SOA\*<sub>process</sub>



PSI SMOG chamber

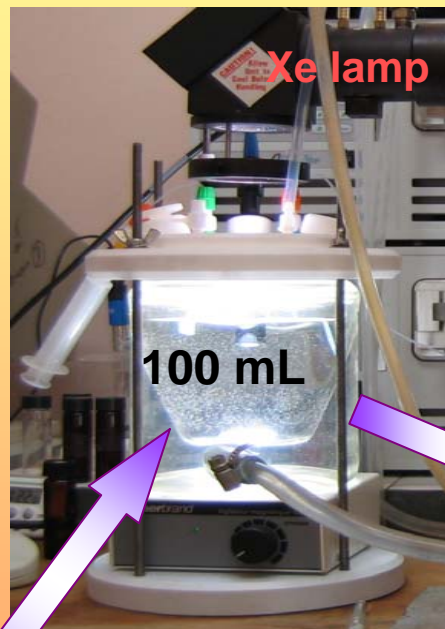


720 L

Filter  
collection



Water  
extraction



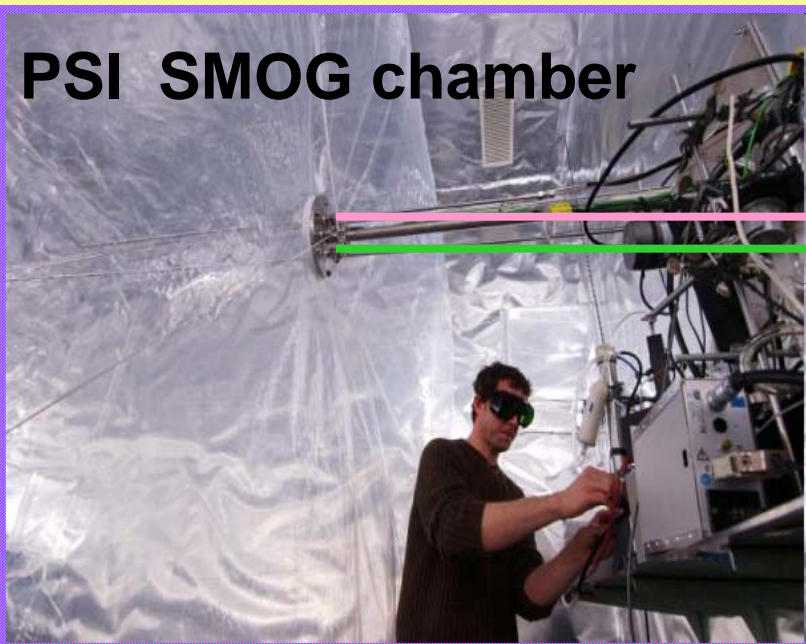
Aqueous  
phase  
photoreactor

Nebulization

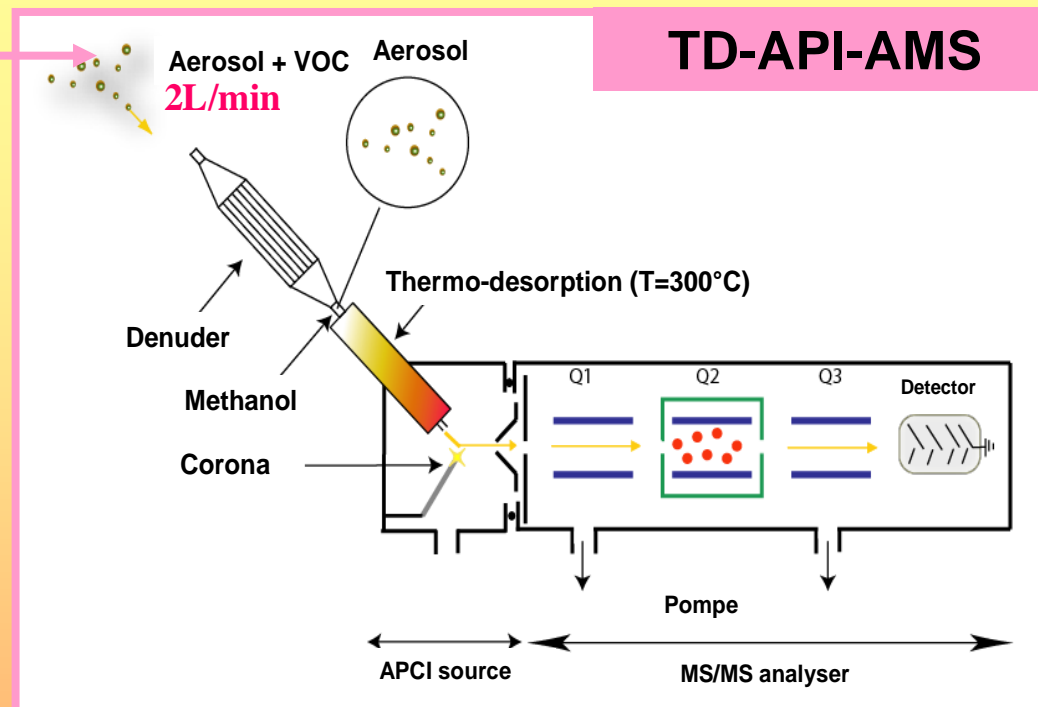
?

# SMOG chamber experimental conditions

## VOC photooxidation



PSI SMOG chamber



TD-API-AMS

On-line analysis of the chemical composition of SOA (Eyglunent *et al.*, 2008)

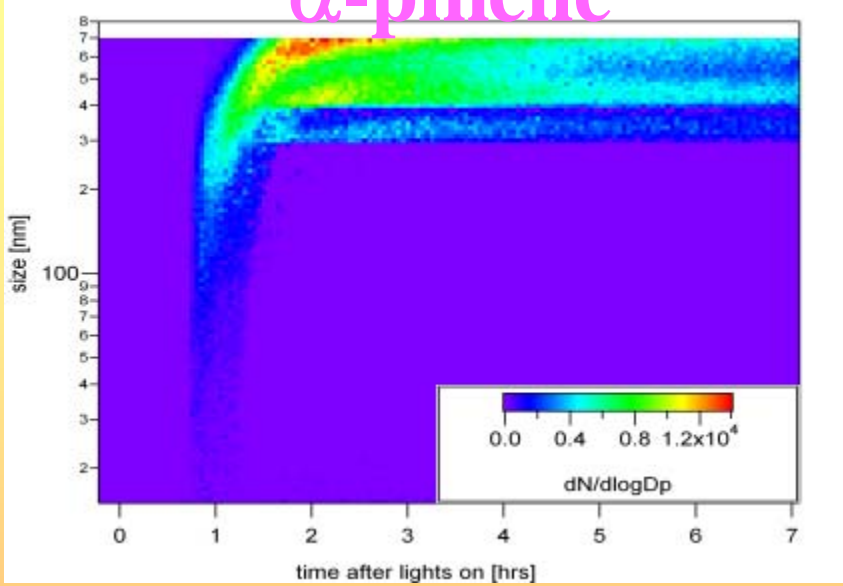
	Initial concentration (ppbv)		RH (%), t°C
	VOC	NOx	
Isoprene	5000	2500	40-50% 25°C
α-pinene	500	250	
1,3,5-TMB	1500	750	

SMPS

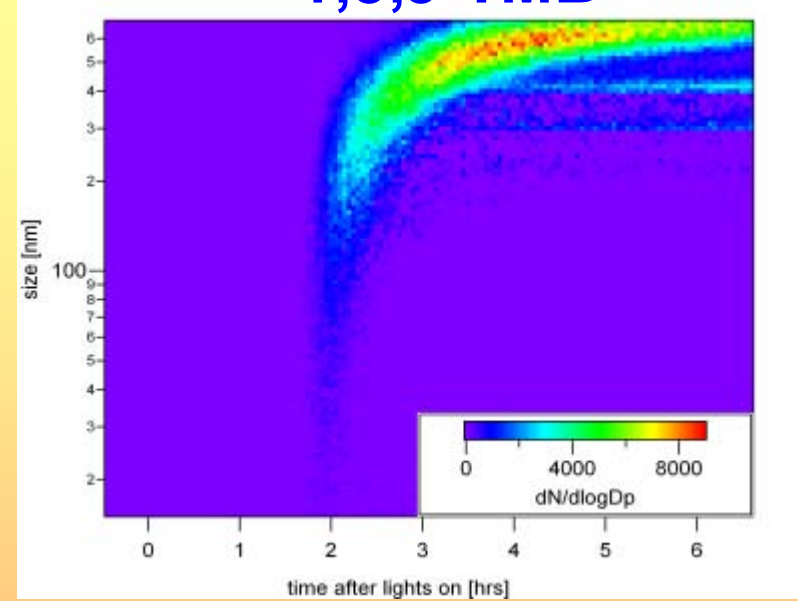
On-line analysis of the granulometric distribution of SOA

# SMOG chamber results

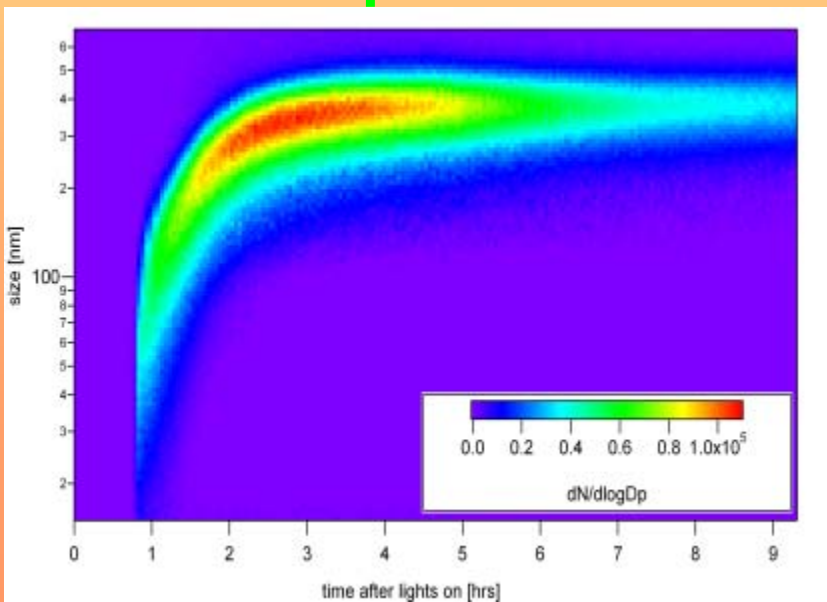
$\alpha$ -pinene



1,3,5-TMB

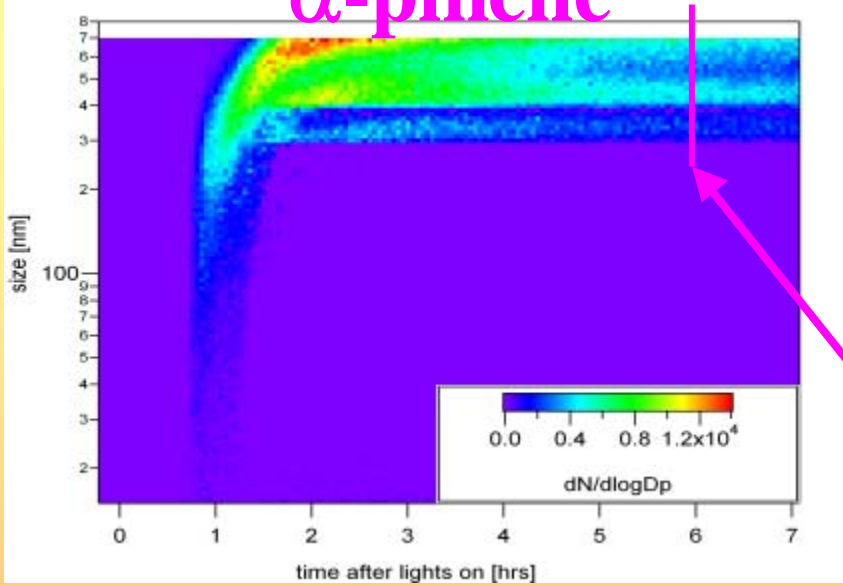


Isoprene

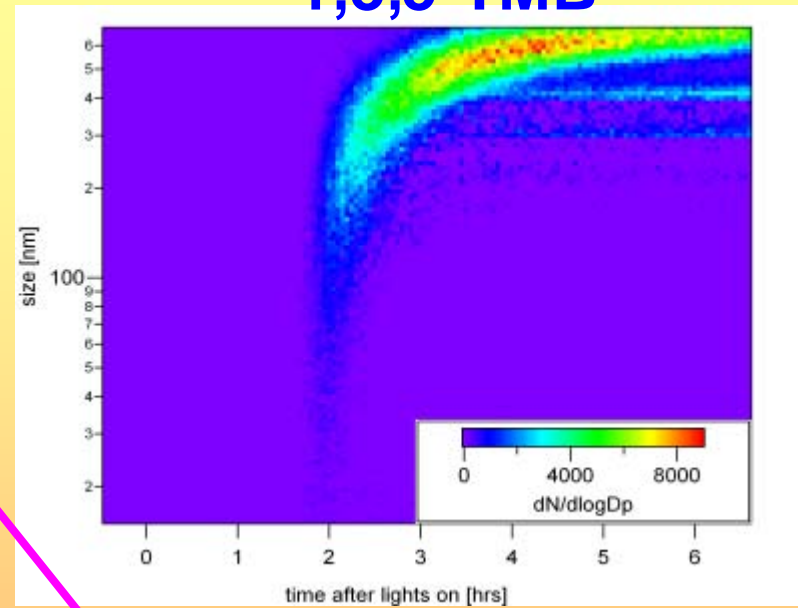


# SMOG chamber results

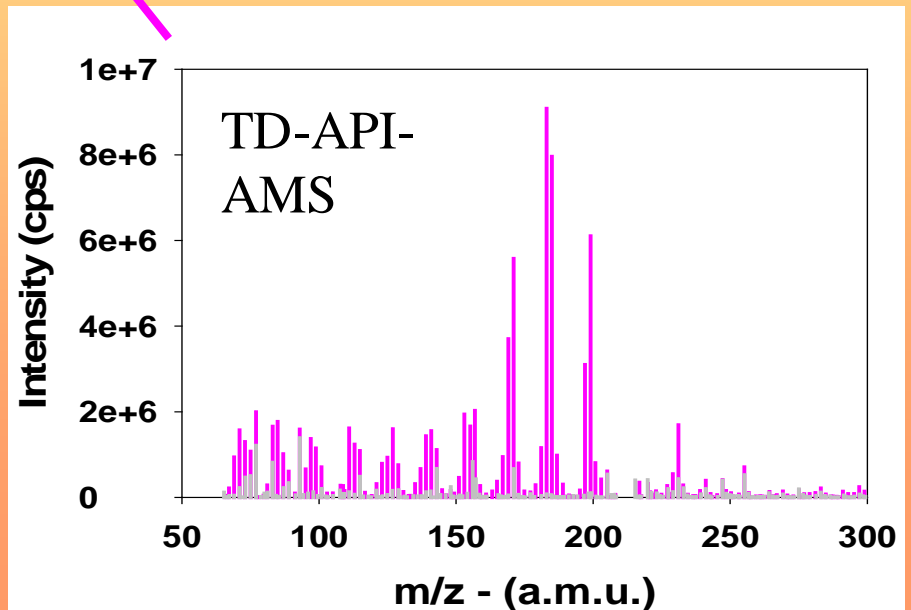
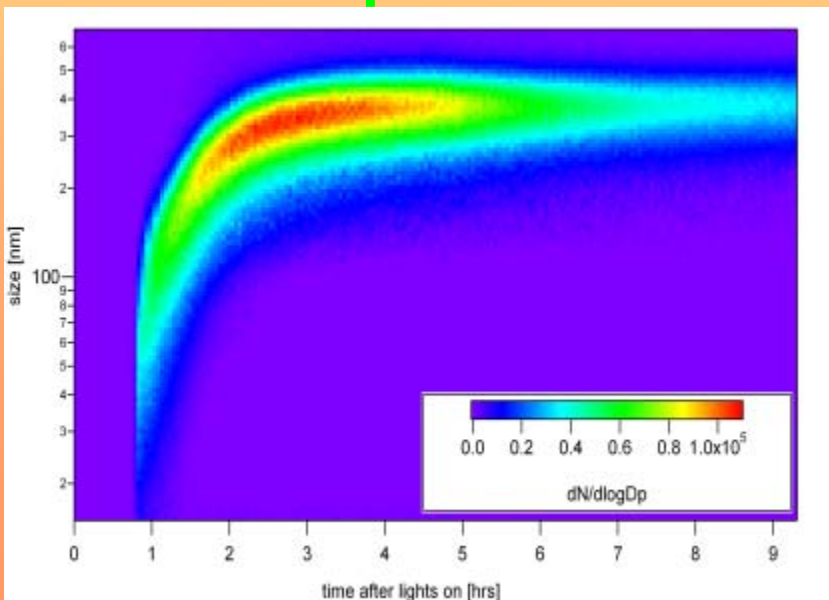
$\alpha$ -pinene



1,3,5-TMB

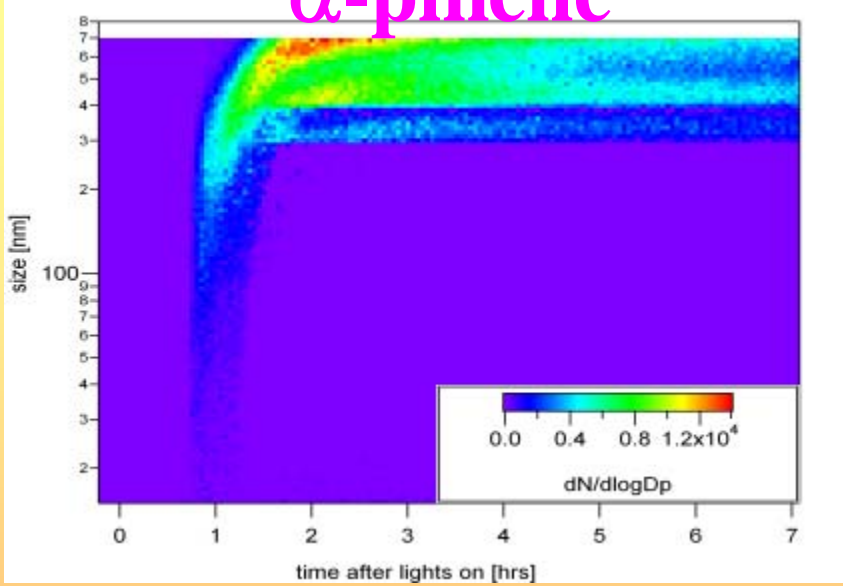


Isoprene

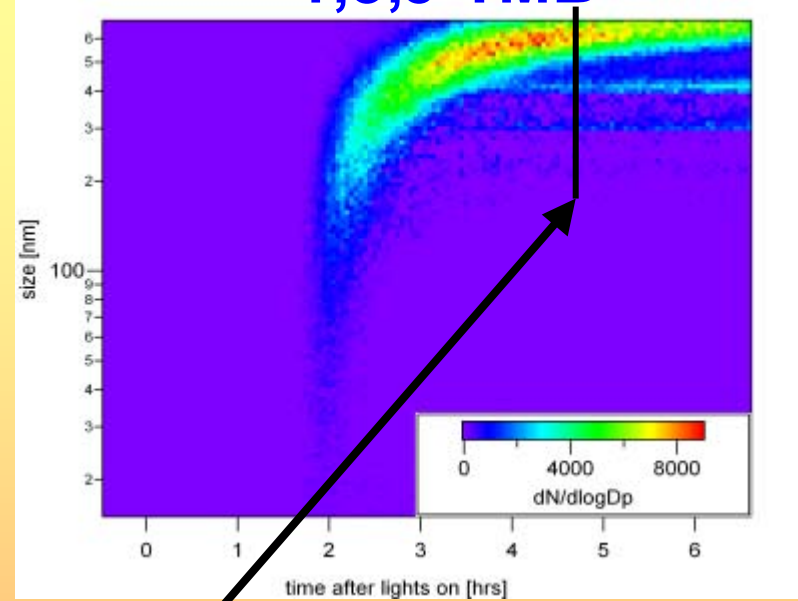


# SMOG chamber results

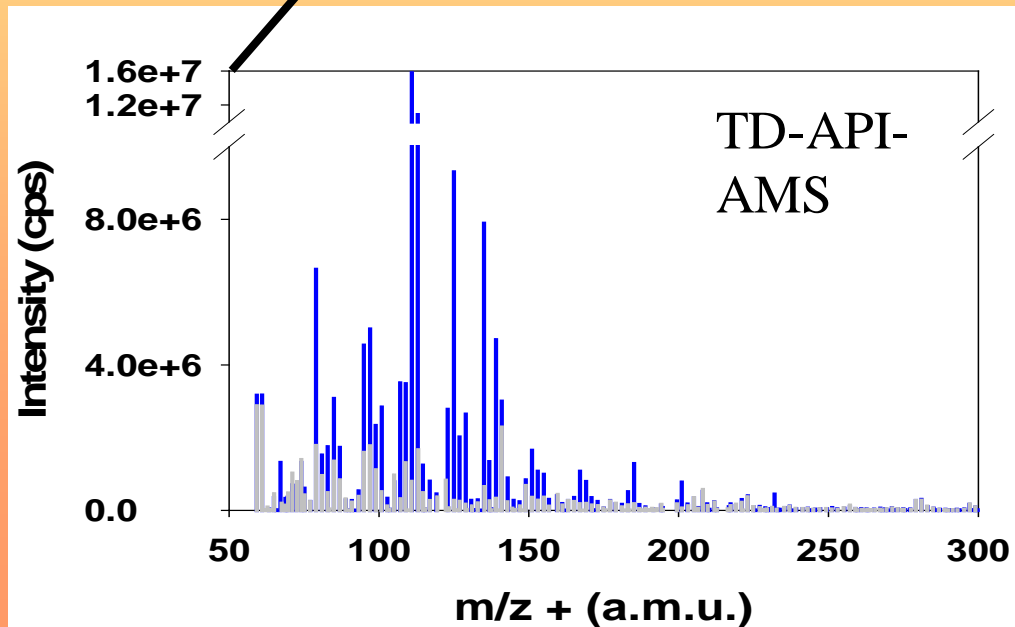
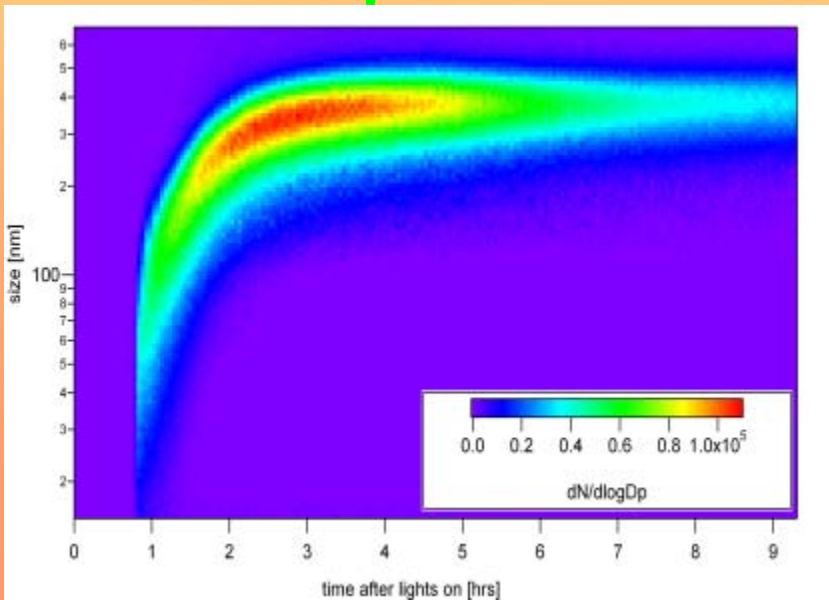
$\alpha$ -pinene



1,3,5-TMB

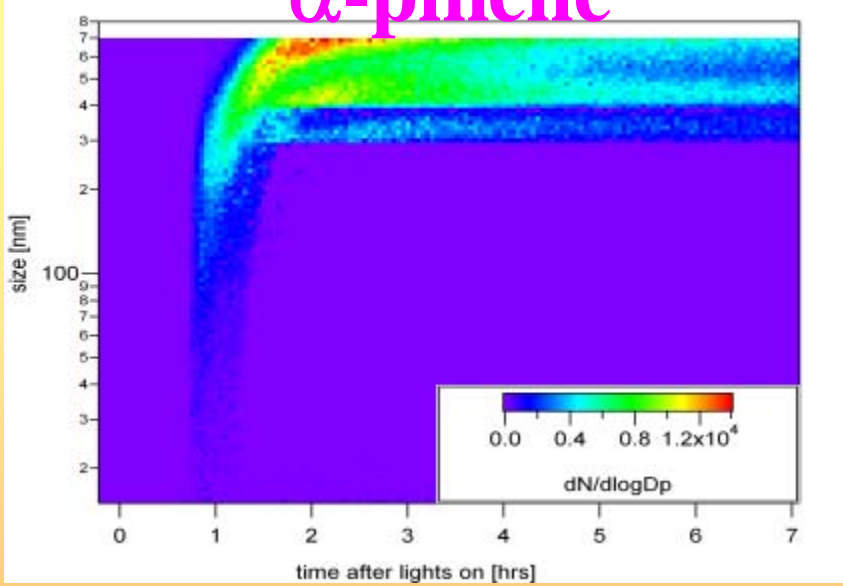


Isoprene

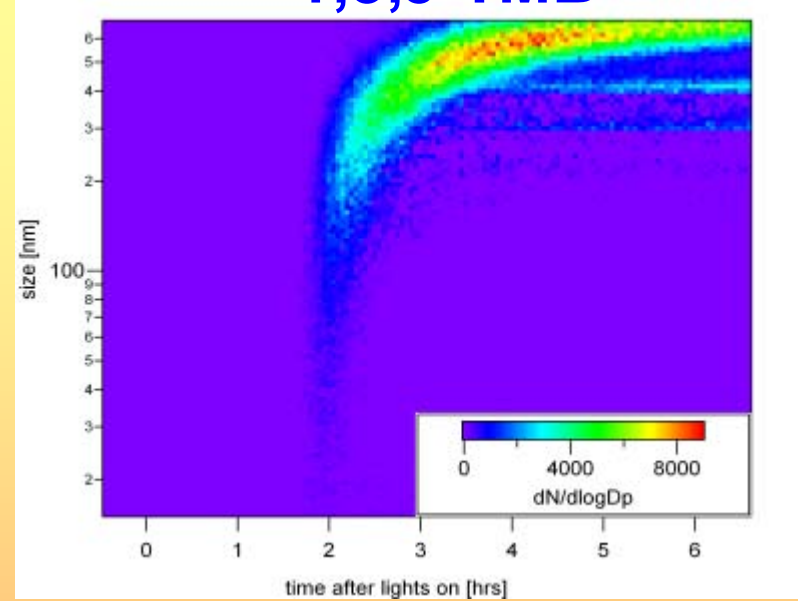


# SMOG chamber results

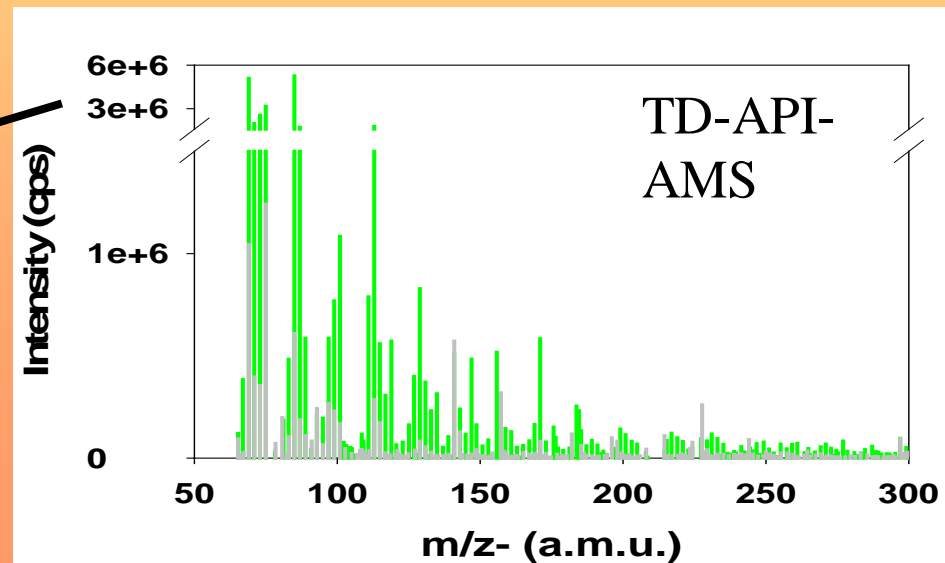
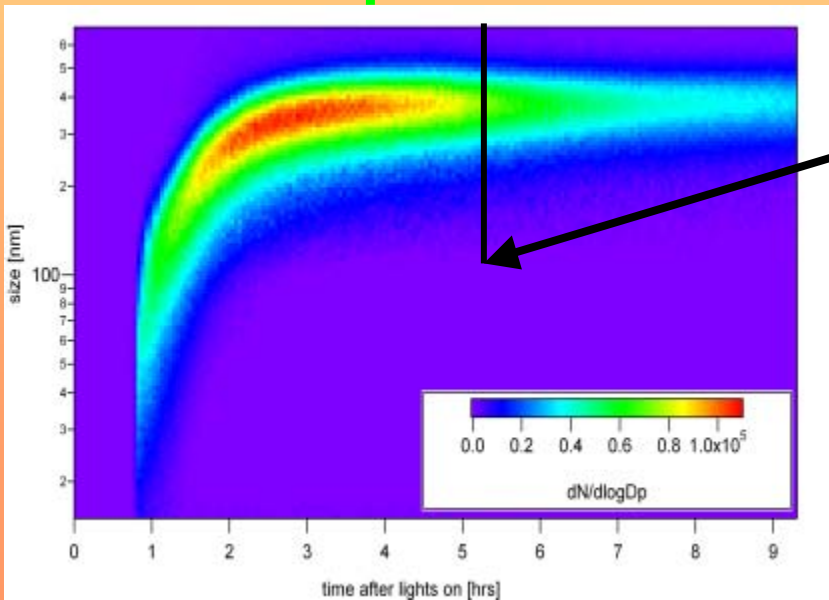
$\alpha$ -pinene



1,3,5-TMB

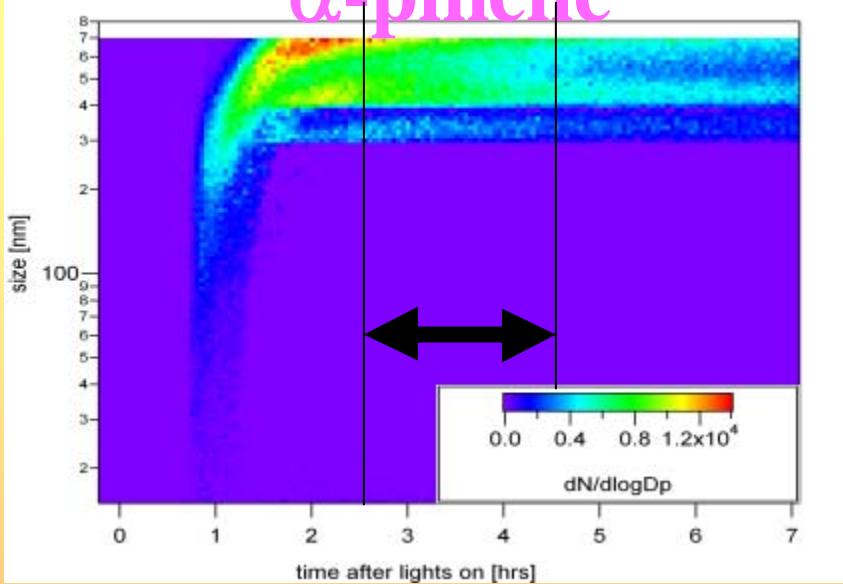


Isoprene

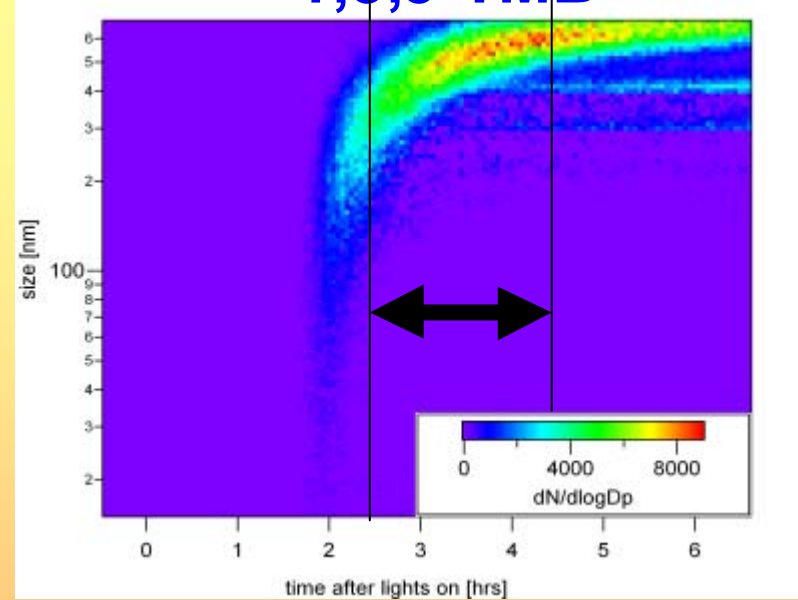


# SMOG chamber : filter collection

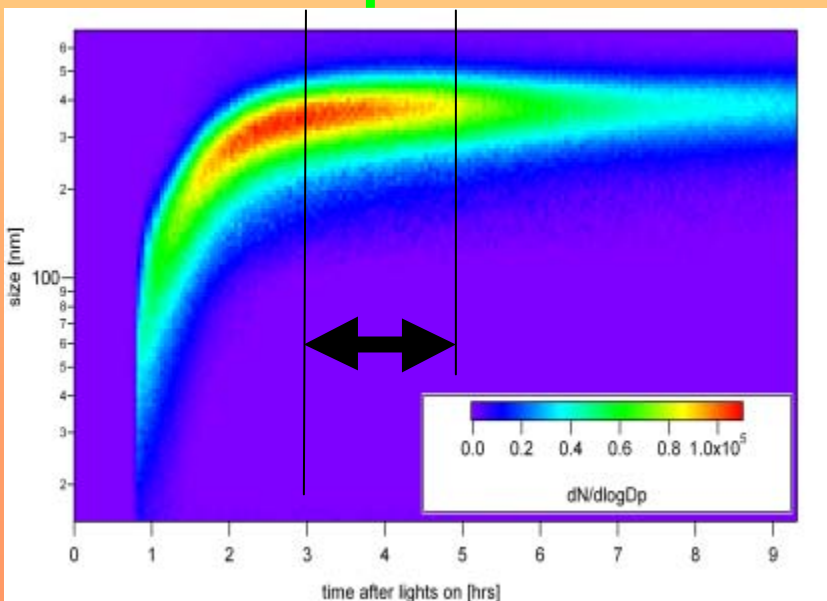
$\alpha$ -pinene



1,3,5-TMB

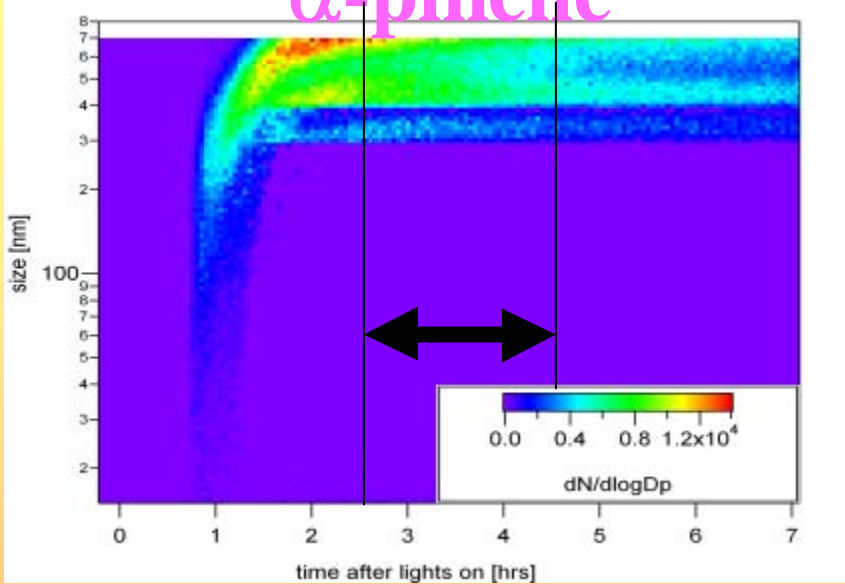


Isoprene

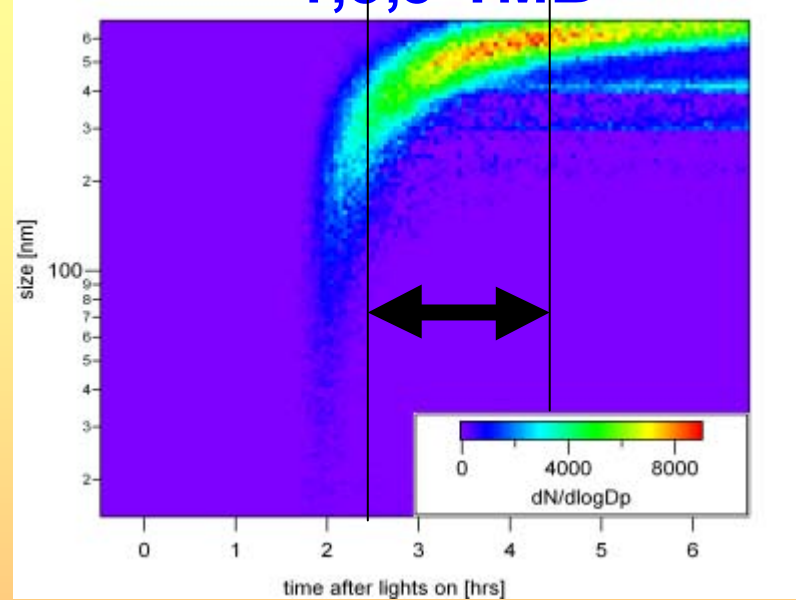


# SMOG chamber : filter collection

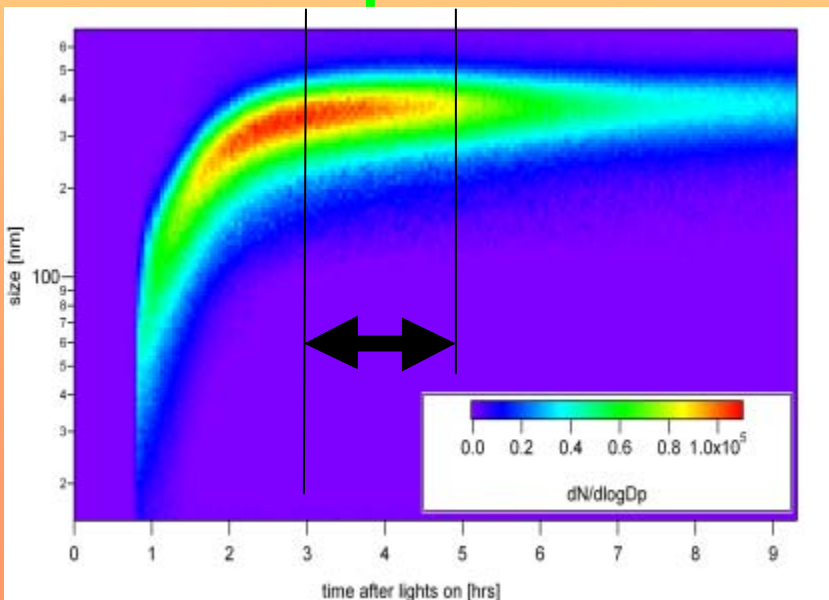
$\alpha$ -pinene



1,3,5-TMB



Isoprene



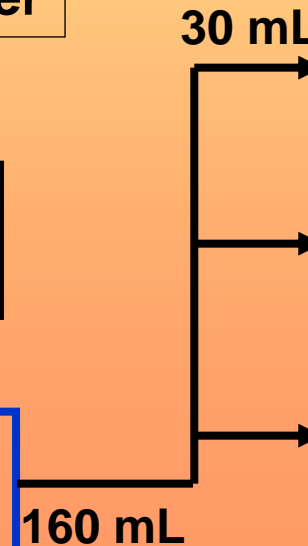
SMOG chamber

720 L

Filter collection

Water extraction 160 mL

30 mL : no process  
Nebulization

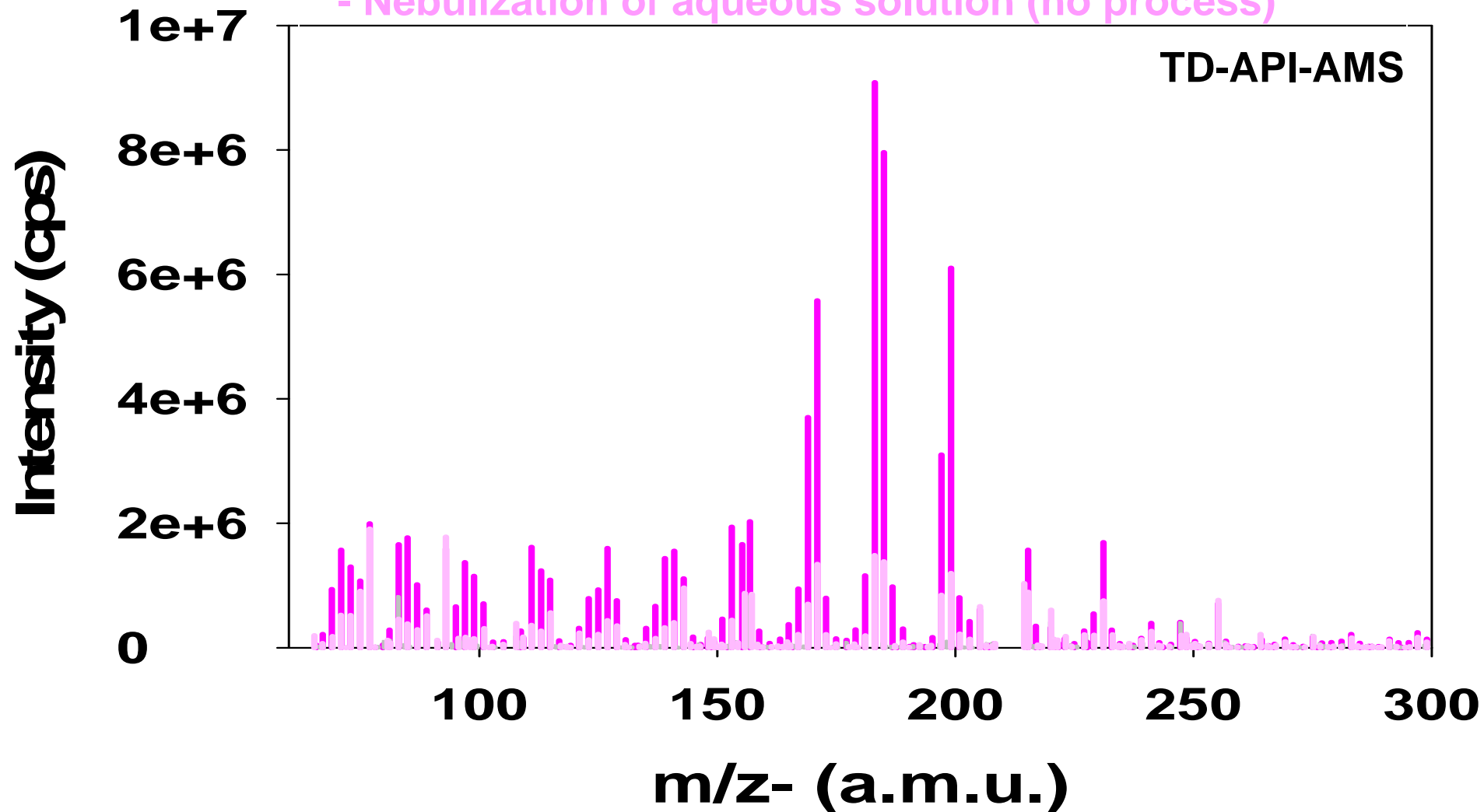


**SOA<sub>no process</sub>**

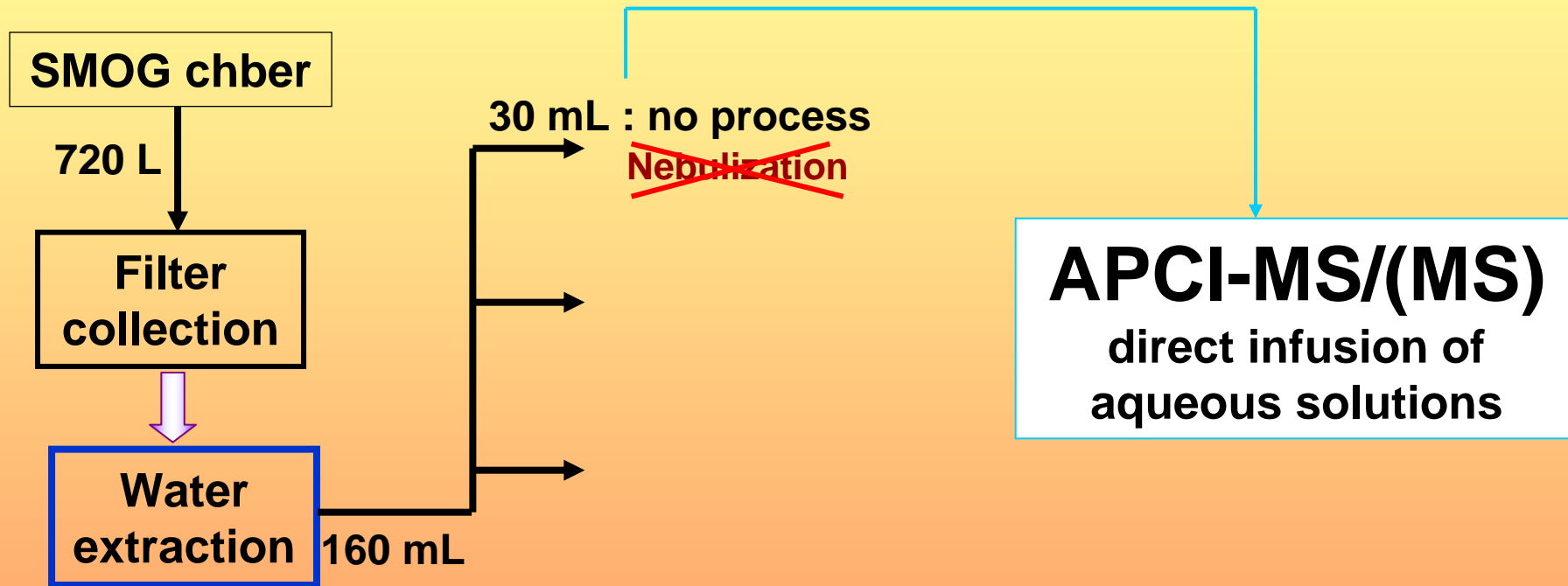
# Nebulization: comparison with SMOG chamber

## $\alpha$ -pinene

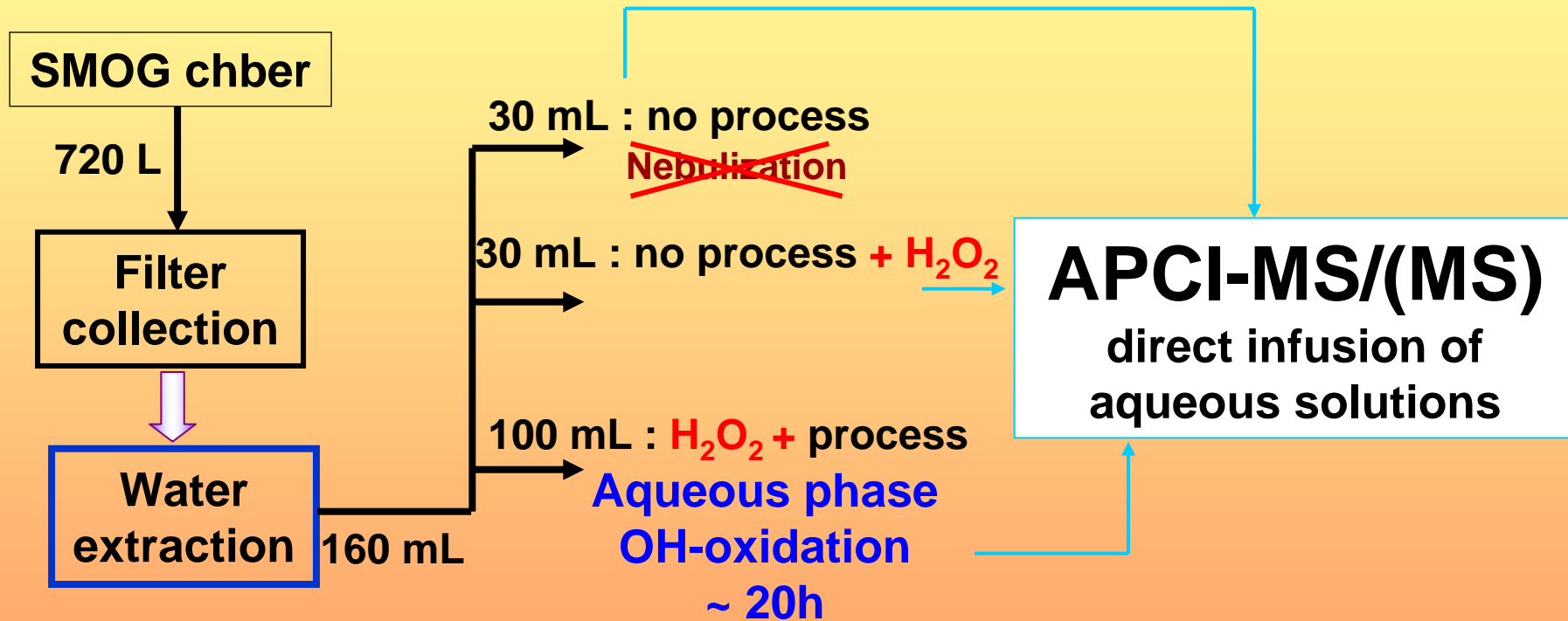
- SMOG chamber (6h05 min)
- Nebulization of aqueous solution (no process)



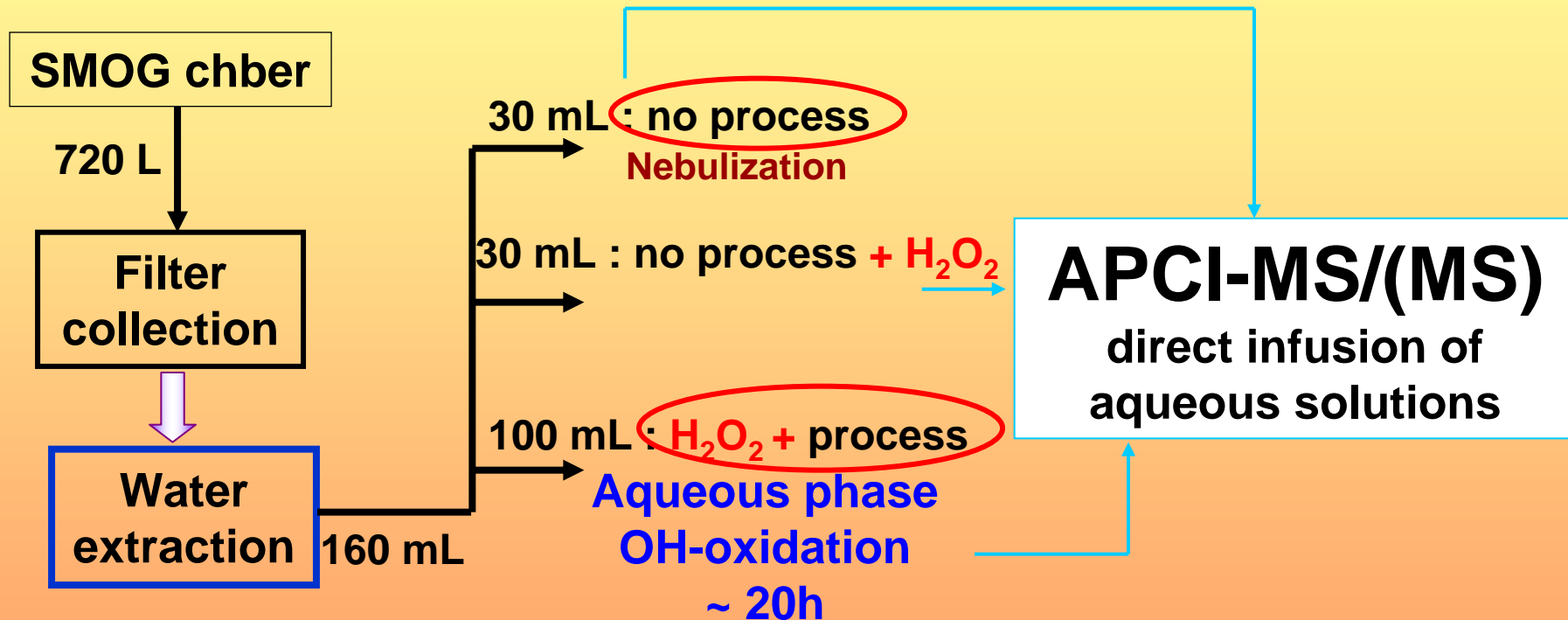
# Water extracts : experimental conditions



# Water extracts : experimental conditions



# Water extracts : experimental conditions

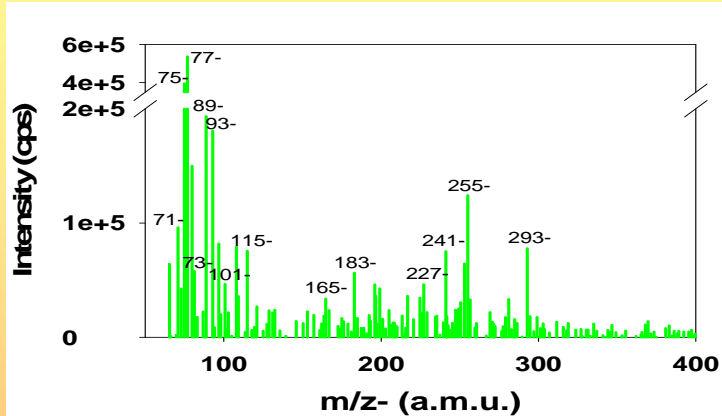


# Comparison $SOA_{no\ process}$ / $SOA^*_{process}$

## Differences of APCI-MS spectra

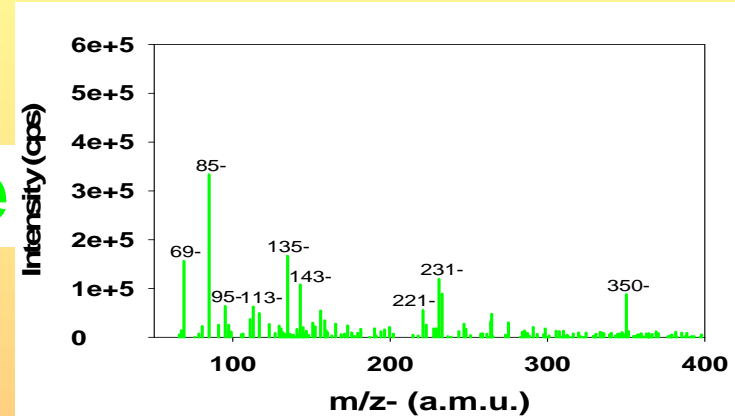
No process - process : ↙

Products' consumption



Process – no process : ↘

Products' formation



Isoprene

# Comparison $SOA_{no\ process} / SOA^*_{process}$

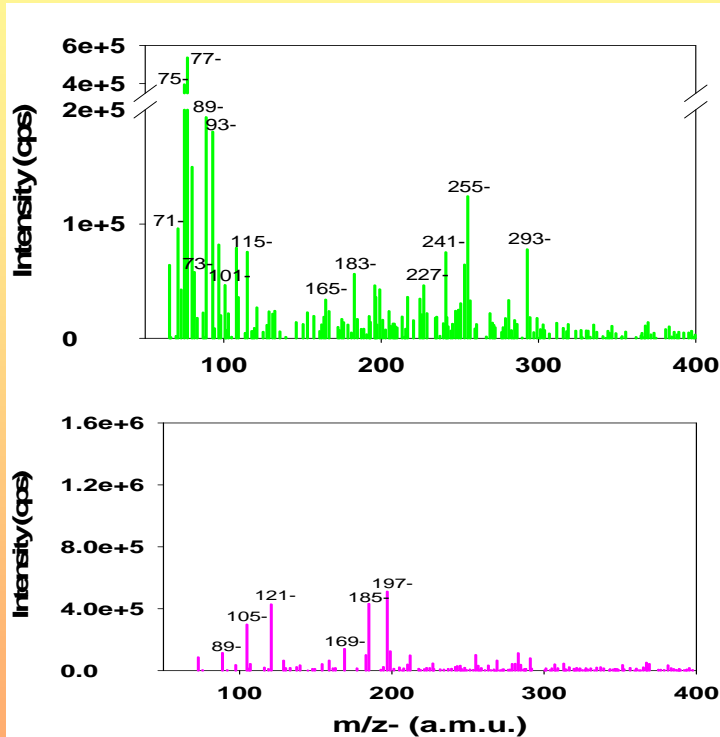
## Differences of APCI-MS spectra

No process - process : ↙

Products' consumption

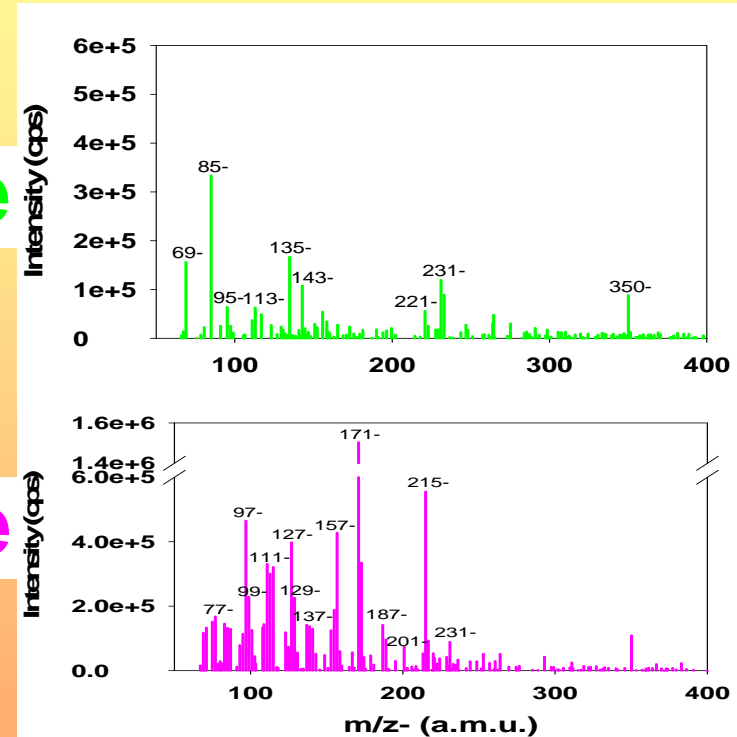
↘ Process – no process :

Products' formation



Isoprene

$\alpha$ -pinene



# Comparison $SOA_{no\ process} / SOA^*_{process}$

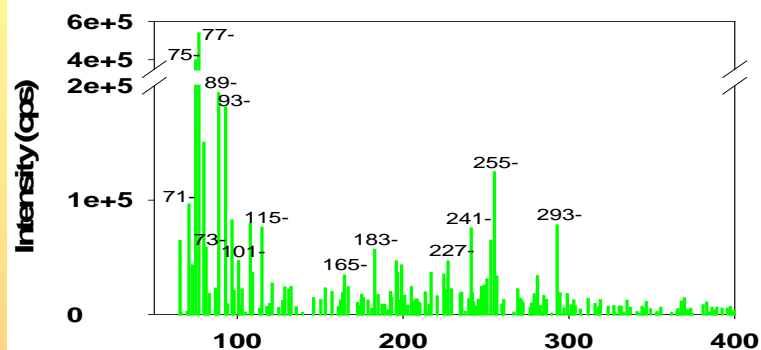
## Differences of APCI-MS spectra

No process - process :

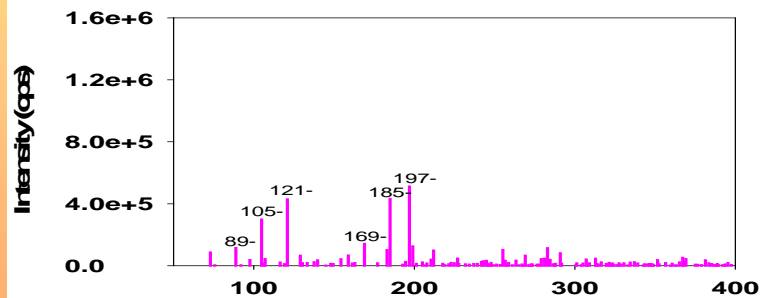
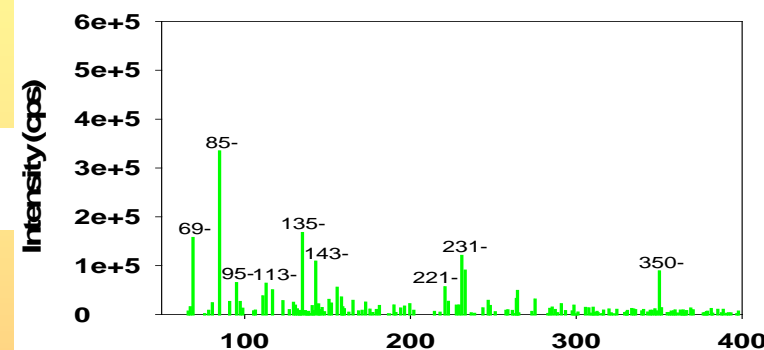
Products' consumption

Process - no process :

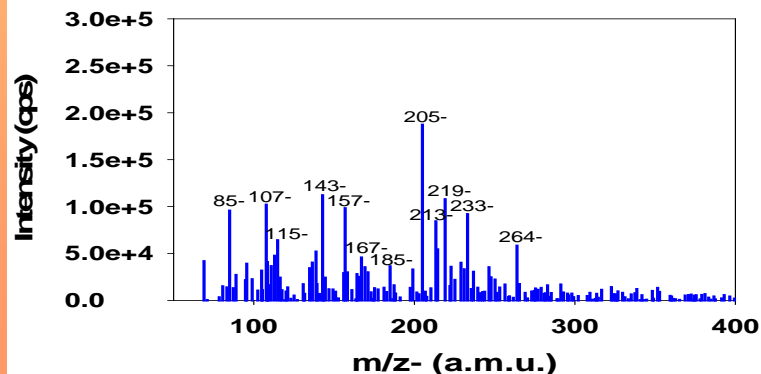
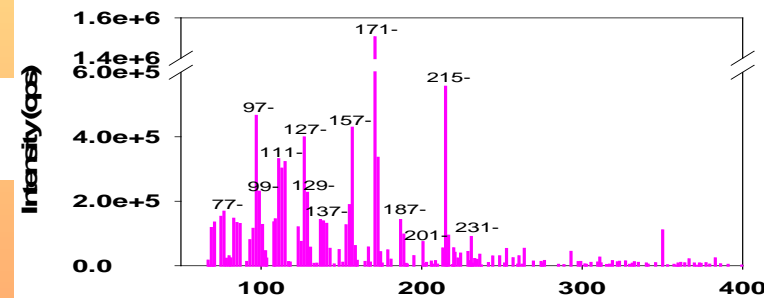
Products' formation



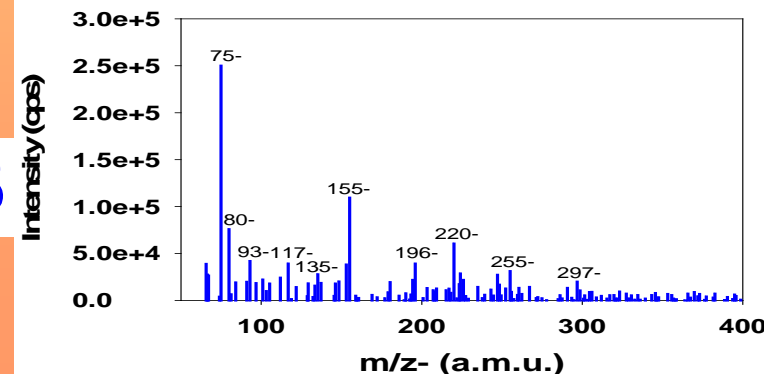
Isoprene



$\alpha$ -pinene



1,3,5-TMB



# Comparison $SOA_{no\ process} / SOA^*_{process}$

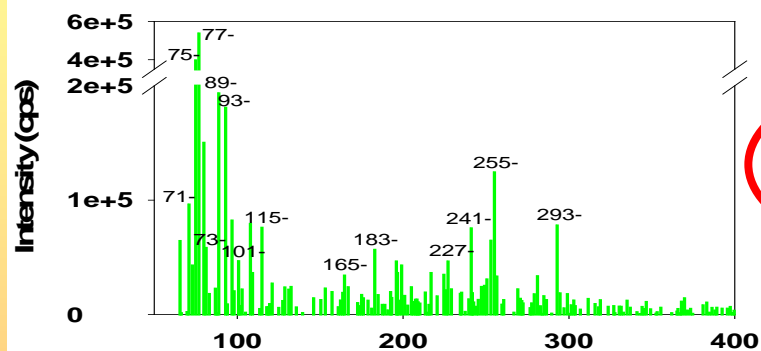
## Differences of APCI-MS spectra

No process - process :

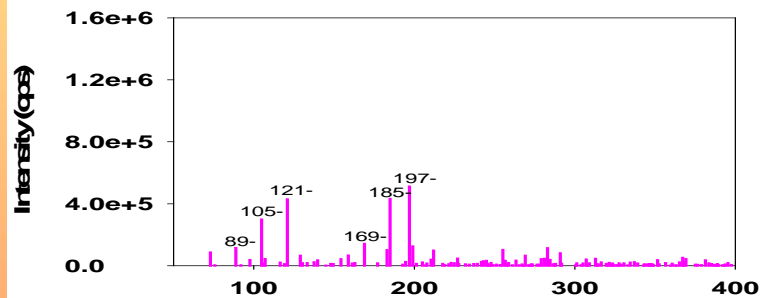
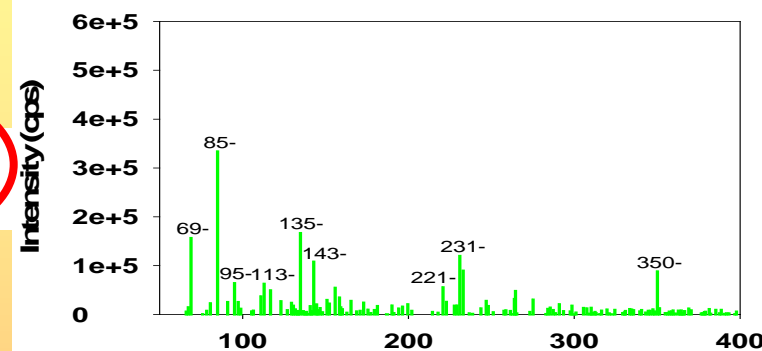
Products' consumption

Process - no process :

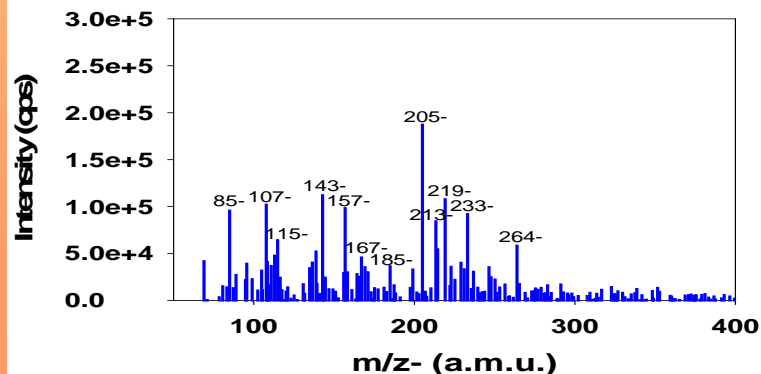
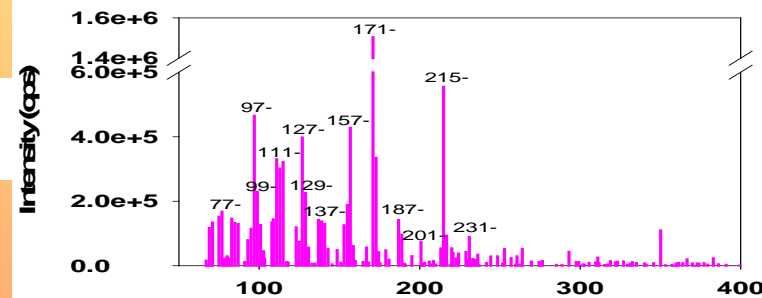
Products' formation



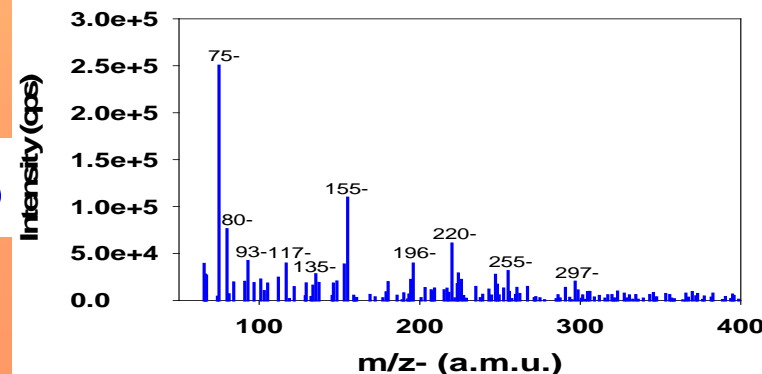
Isoprene



$\alpha$ -pinene

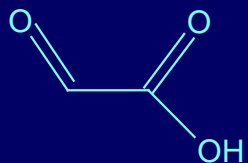


1,3,5-TMB

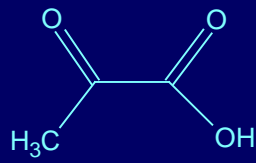


# Isoprene : SOA products' identification study

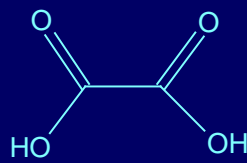
## APCI-MS/MS : identification compounds with standards



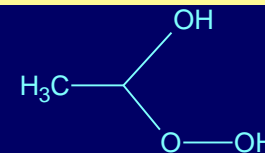
Glyoxylic acid  
m/z= 74



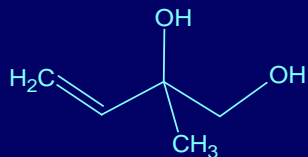
Pyruvic acid  
m/z=88



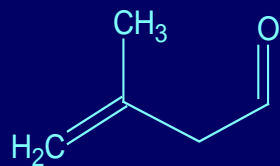
Oxalic acid  
m/z=90



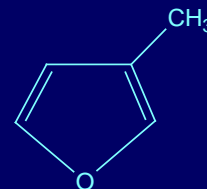
1-Hydroxyethyl-  
hydroperoxide  
m/z=65



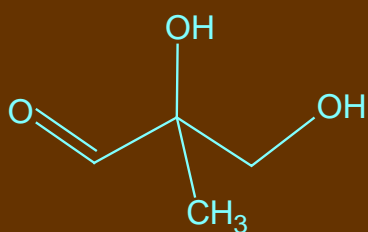
2-methylbut-3-  
ene-1,2-diol  
m/z=102



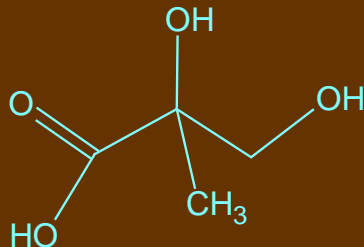
3-methylbut-3-enal  
m/z=84



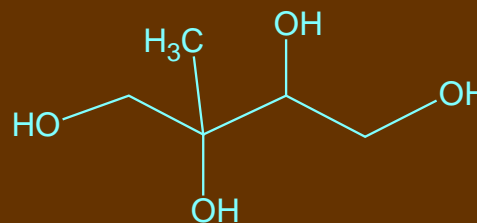
3-methylfuran  
m/z=82



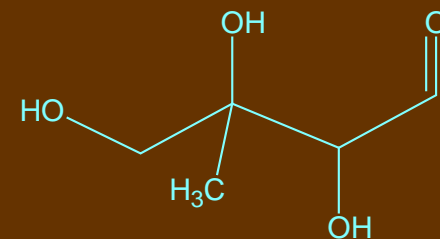
2,3-dihydroxy-2-  
methyl-propanal  
(DMP) m/z=104



2,3-dihydroxy-  
methacrylic acid  
(DMA) m/z=120

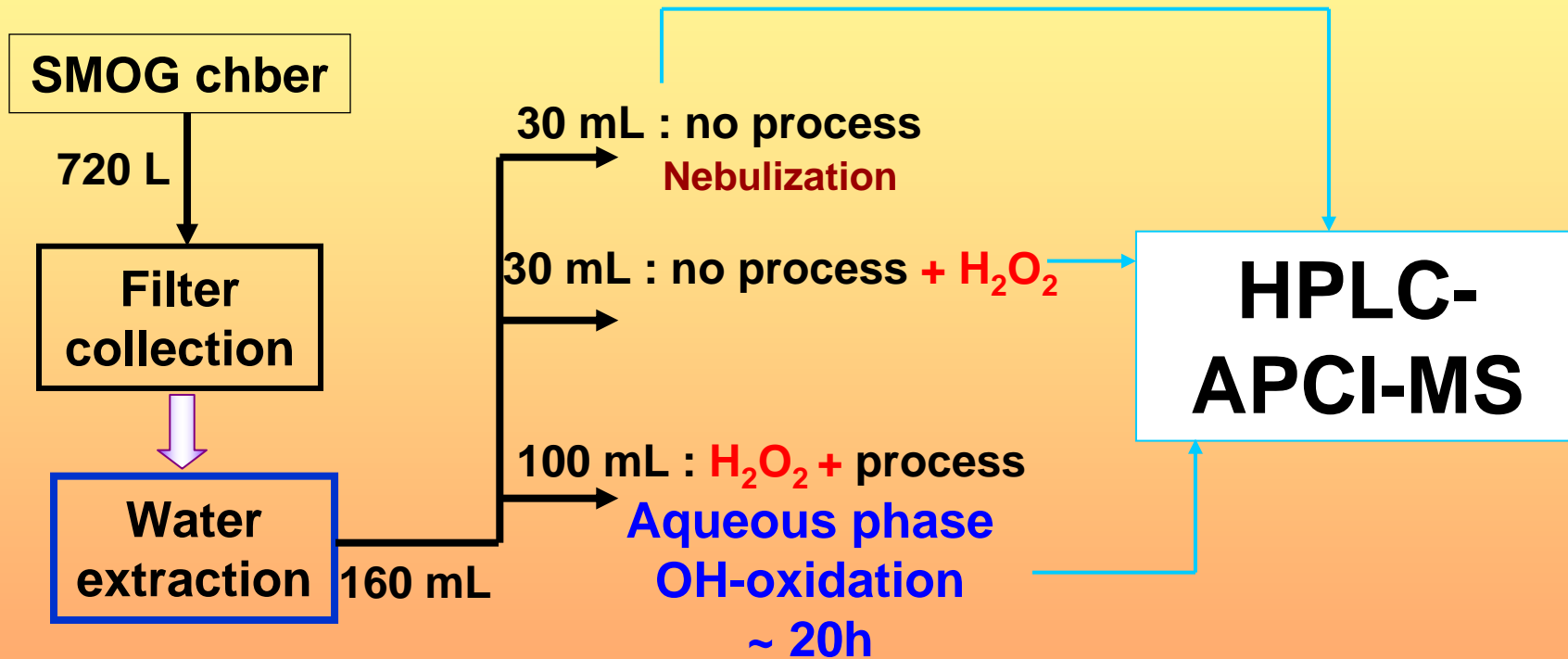


2-methylbutane-  
1,2,3,4-tetrol  
m/z=136



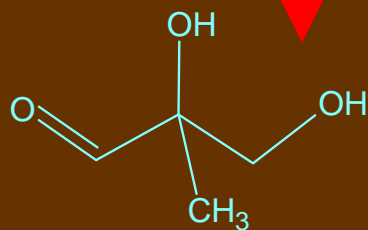
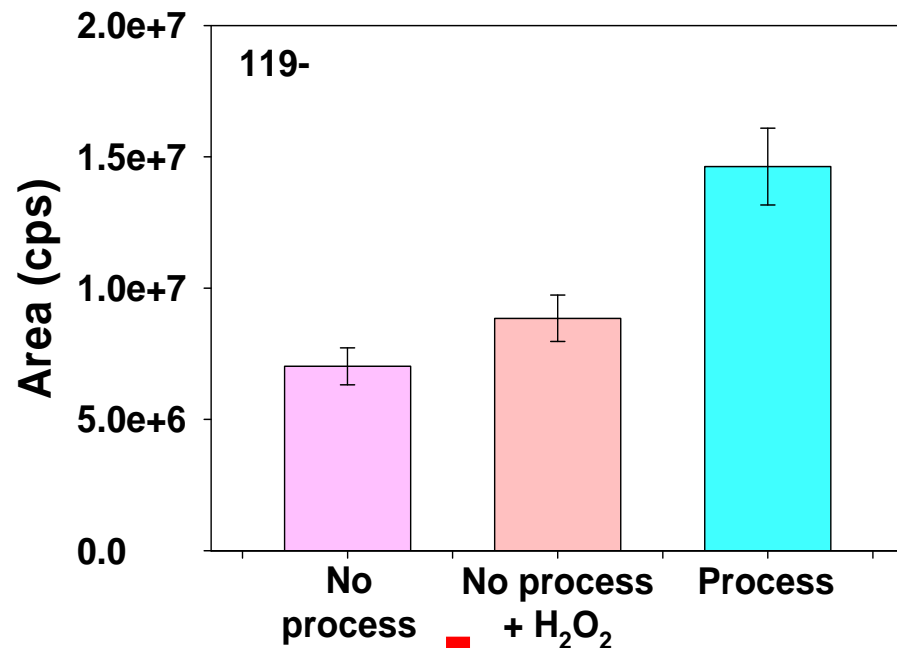
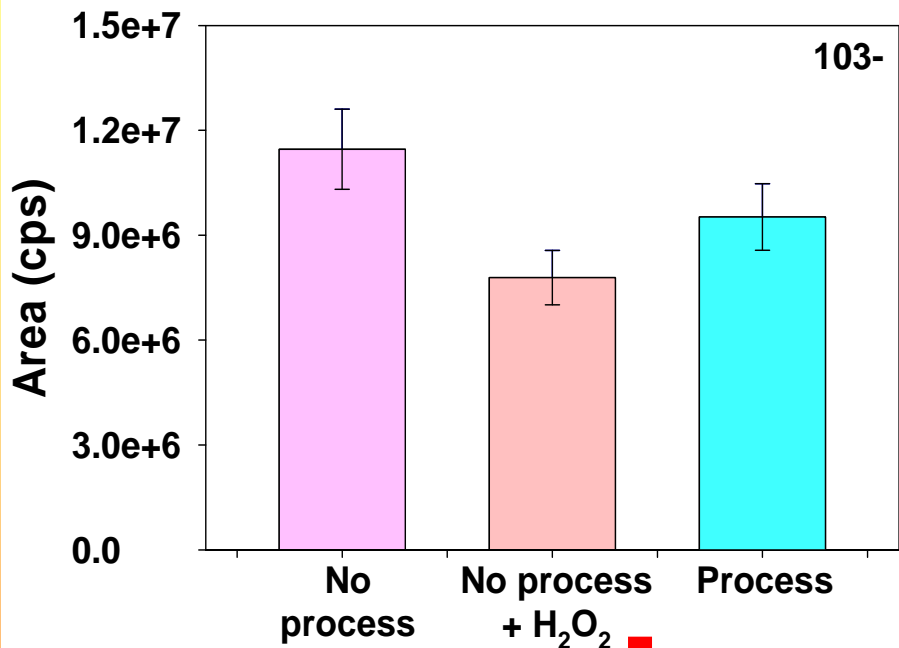
Trihydroxy-3-  
methylbutanal  
(TMB) m/z=134

# Isoprene : SOA products' identification study



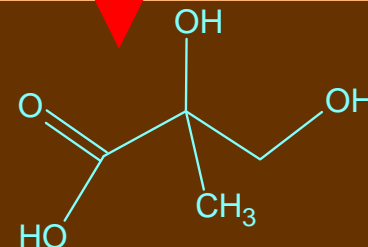
# Isoprene : SOA products' identification study

## HPLC-APCI-MS



2,3-dihydroxy-2-methyl-propanal (DMP) m/z=104

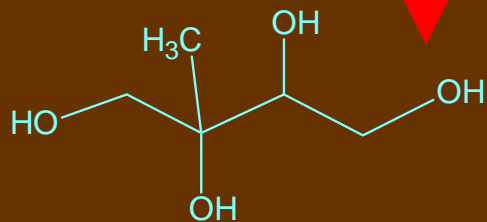
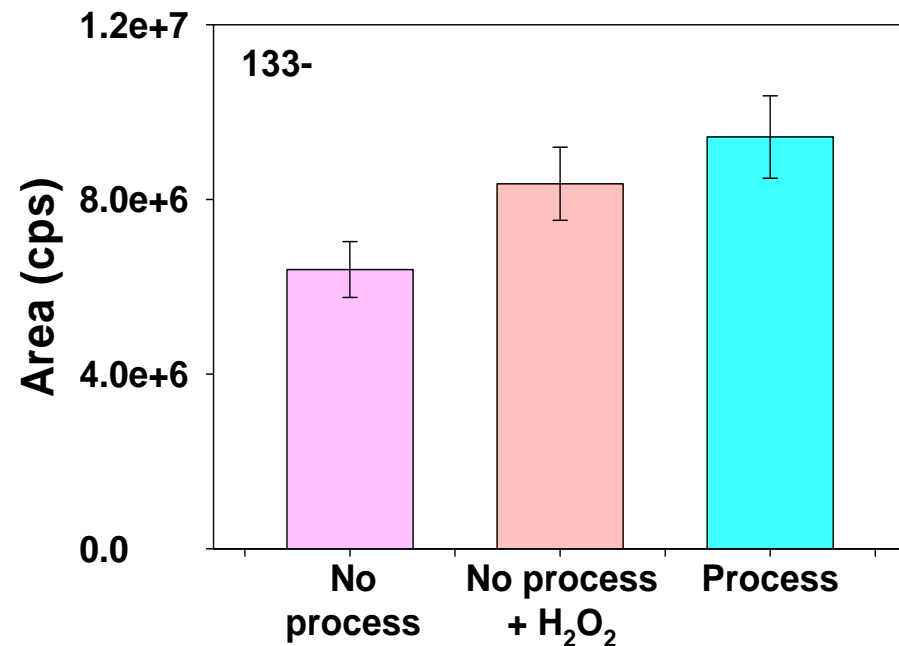
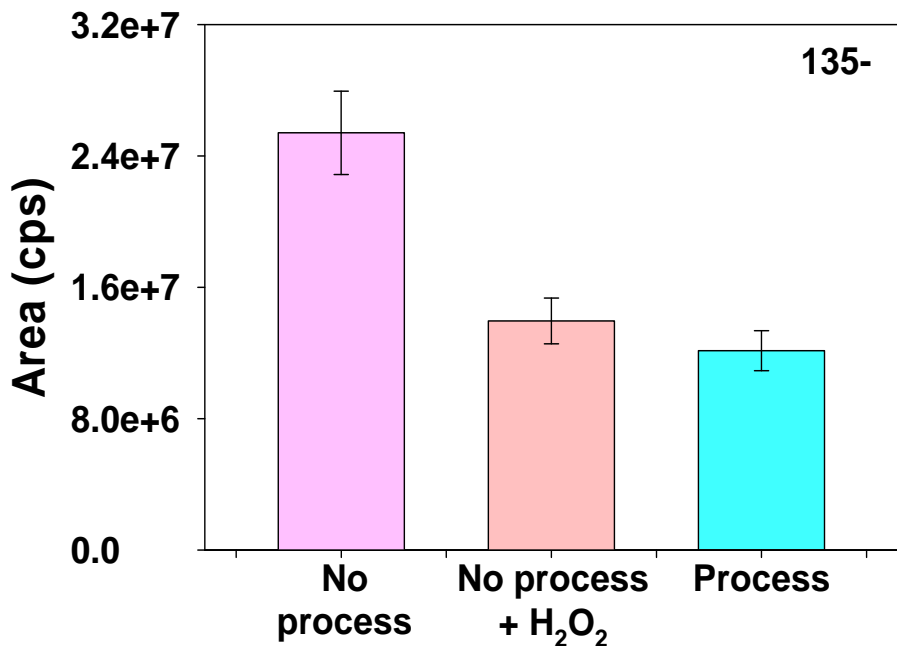
**Aqueous phase  
(photo)oxidation**



2,3-dihydroxy-methacrylic acid (DMA) m/z=120

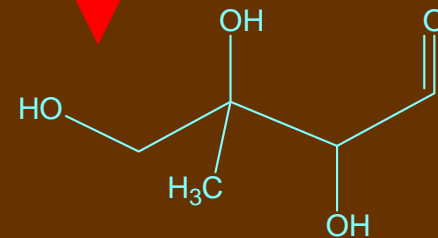
# Isoprene : SOA products' identification study

## HPLC-APCI-MS



2-methylbutane-  
1,2,3,4-tetrol  
m/z=136

**Aqueous phase**  
**(photo)oxidation**



Trihydroxy-3-  
methylbutanal  
(TMB) m/z=134

# Conclusions

## *Preliminary study*

- **Aqueous phase processes can significantly modify the chemical composition of SOA.**
- **The importance of these modifications seem to largely depend on the precursor VOC.**
- **Other properties of these SOA (volatility, hygroscopicity, and chemical composition as a function of particle size) will be treated in the near future.**

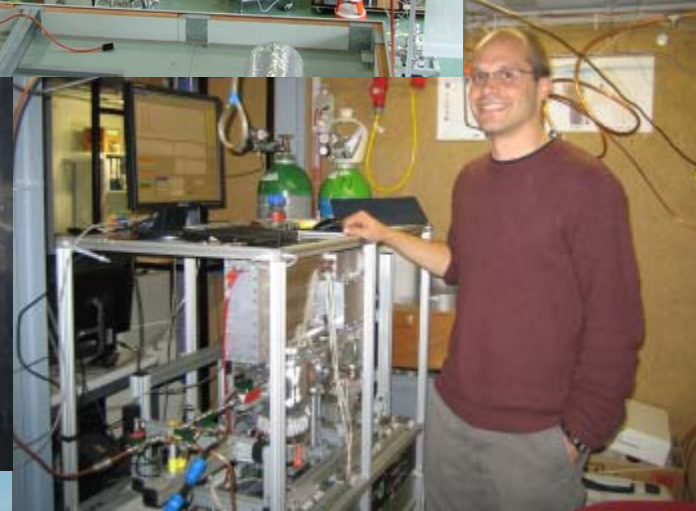
# Aknowledgements

ESF - INTROP

INSU - LEFE - CHAT



EUROCHAMP



SOA<sub>no process</sub>

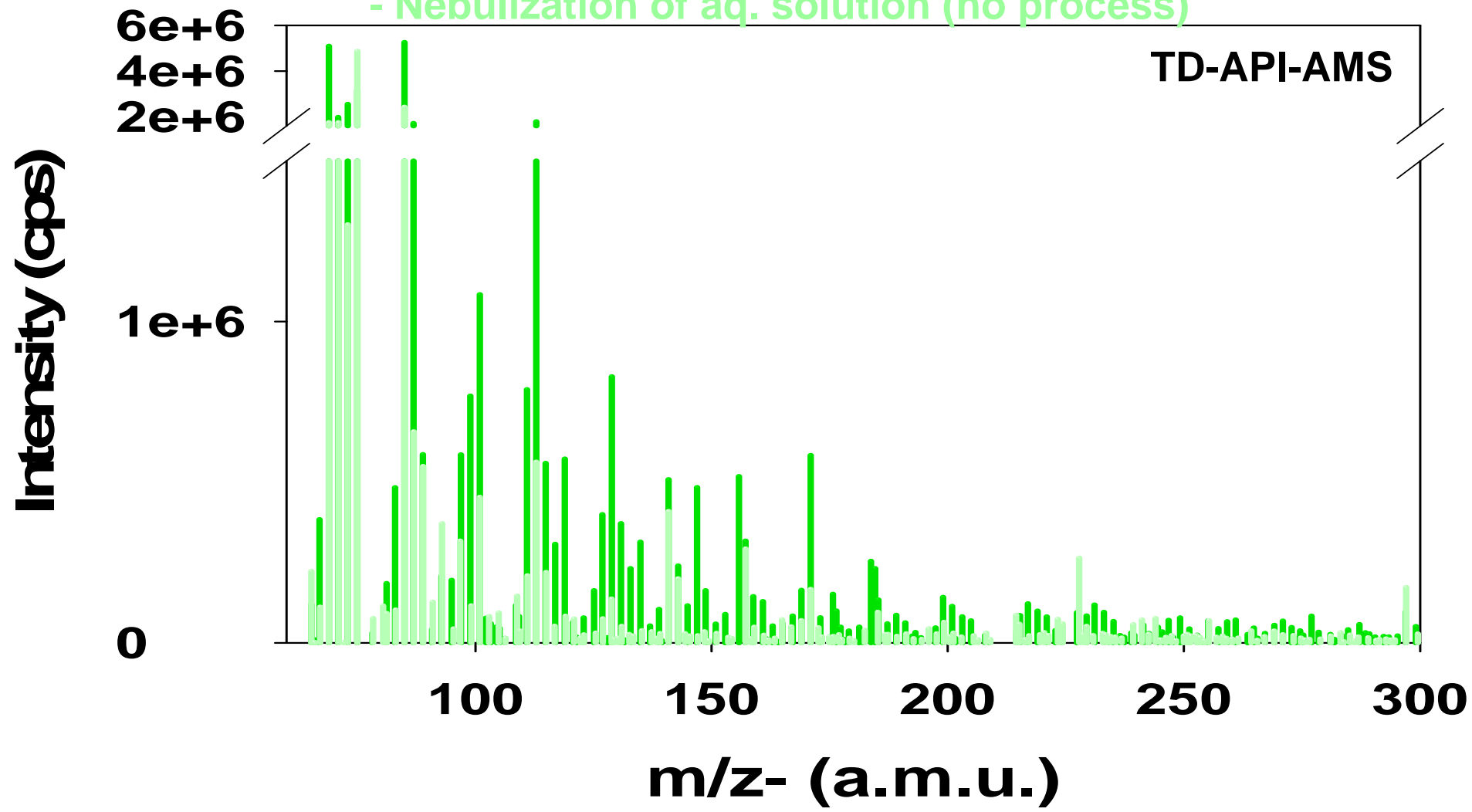
# Nebulization: comparison with SMOG chamber

## Isoprene

- SMOG chamber (5h20 min)

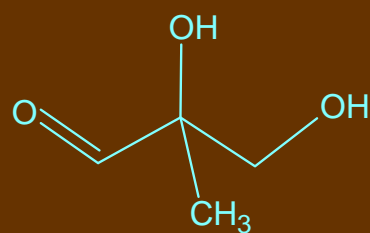
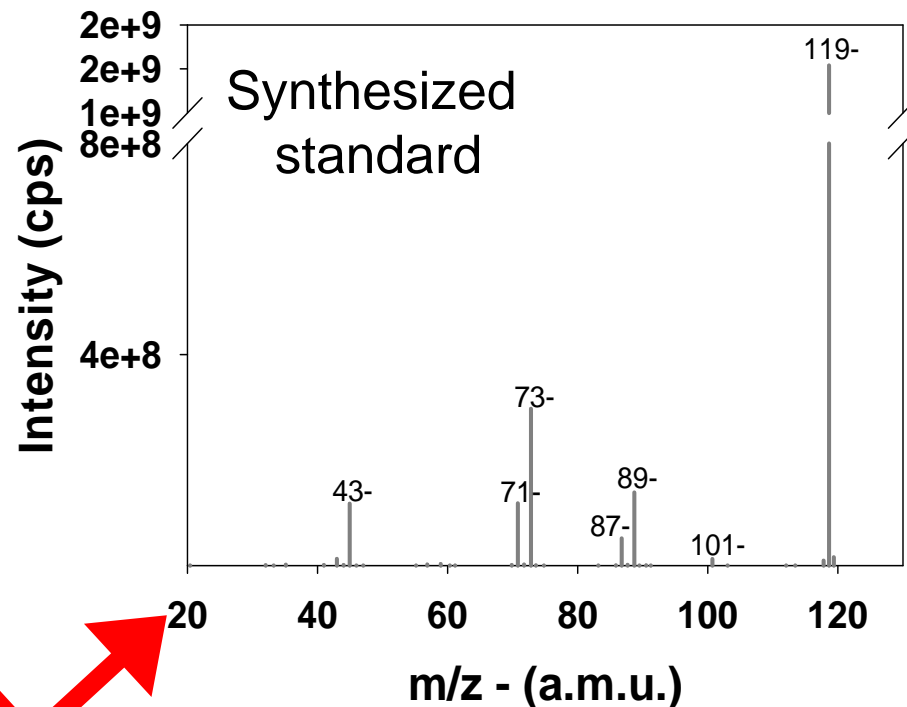
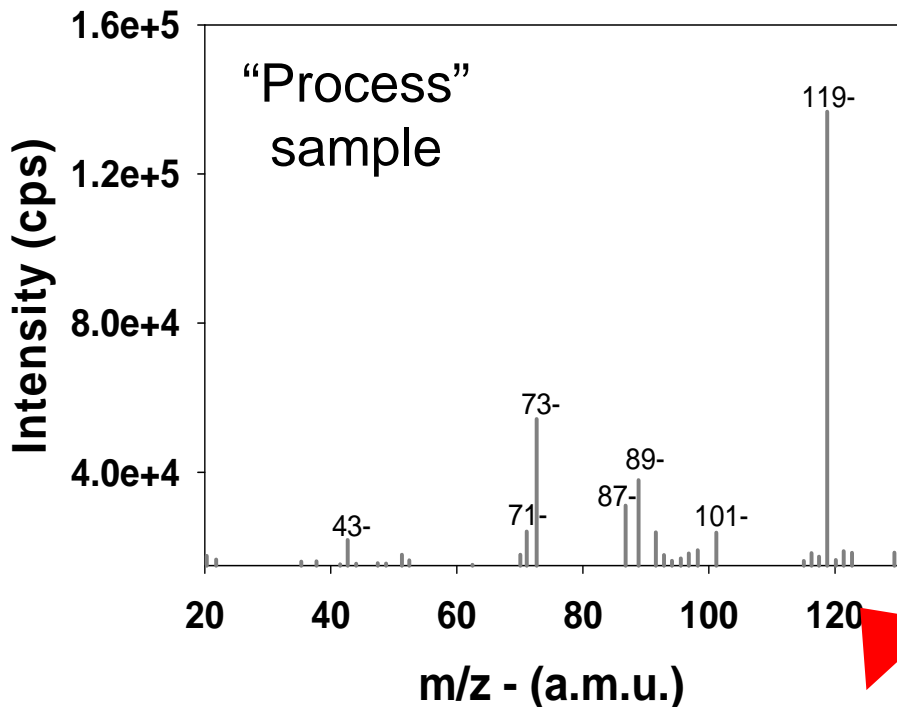
- Nebulization of aq. solution (no process)

TD-API-AMS

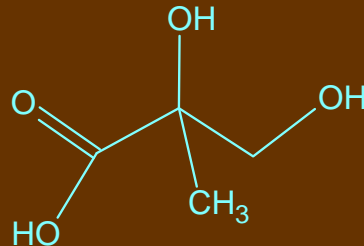


# Isoprene : SOA products' identification study

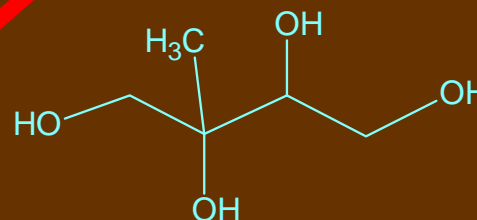
APCI-MS/MS : identification compounds with standards



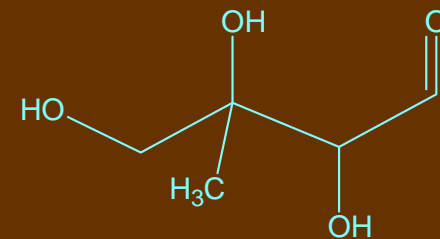
2,3-dihydroxy-2-methyl-propanal (DMP) m/z=104



2,3-dihydroxy-methacrylic acid (DMA) m/z=120



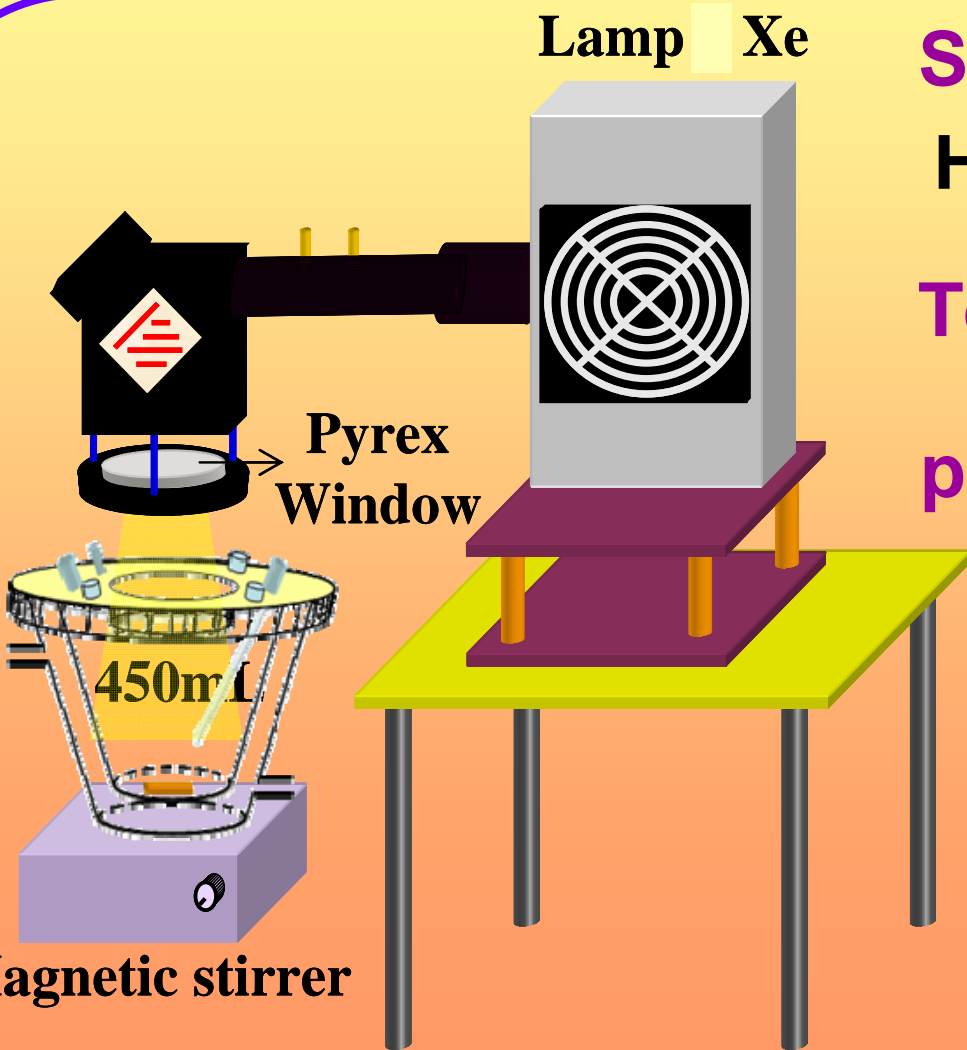
2-methylbutane-1,2,3,4-tetrol m/z=136



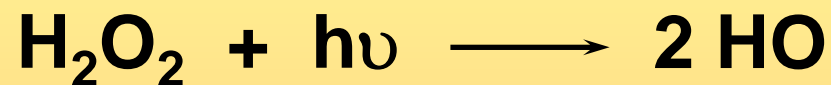
Trihydroxy-3-methylbutanal (TMB) m/z=134

## Aqueous phase experimental conditions

	Sample volume (ml)			[H <sub>2</sub> O <sub>2</sub> ] (M)	Reaction time (h)
	No process (OH of reaction)	No process + H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> + hv process		
<b>Isoprene</b>	30	30	100	0.1	20
<b>α-pinene</b>	30	---	100	1.5 x 10 <sup>-2</sup>	21
<b>1,3,5-TMB</b>	30	30	100	4.5 x 10 <sup>-2</sup>	20



Source of OH :



Temperature : 25 °C

pH : "free" (not buffered)

Aqueous phase  
photoreactor