

# Chemical Reactivity of Soot and Secondary Organic Aerosols generated under Laboratory Conditions

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## *Introduction*

Today, large uncertainties persist concerning the impact of aerosols on the radiative forcing owing to the very low level of scientific understanding of the mechanisms involved (fig. 1). Radiative forcing due to aerosols not only depends on its spatial distribution, but also on the size, shape, and chemical composition of the particles. This is the reason for the present effort which intends to characterize the surface functional groups of aerosol particles generated under well controlled conditions as these groups primarily interact with atmospheric gases. This work is focused on soot and on Secondary Organic Aerosols that come both from anthropogenic sources and are present in the same quantities in the troposphere ( $\cong 10 \text{ Tg yr}^{-1}$ ). We have chosen toluene as a precursor since it is the most abundant aromatic compound in urban air ( $\cong 6 \%$  of the observed non methane hydrocarbons).

## *Experimental setup*

Soot samples are produced in a reproducible way from liquid toluene ( $\text{C}_7\text{H}_8$ ) using a co-flow system (fig.2). SOA particles are generated from the photo-oxidation of toluene in the presence of  $\text{O}_3$  at 1 atmosphere of humid air (90% r.h.) using a 150W high-pressure Xe arc lamp. The SOA production is taking place in an atmospheric pressure flow cell (fig. 3) whose gas phase is monitored using a differentially pumped Quadrupole Mass Spectrometer (BALZERS, QMS 200). The flow is passed across a PTFE filter (MILLIPORE, 0.2  $\mu\text{m}$  pore diameter) during one to two hours at constant throughput leading to typical collected sample masses of a few mg. The size distribution of SOA has been characterized by a Scanning Mobility Particle Sizer (TSI, 3071 A / 3022 A). Finally, FTIR Photo-acoustic Spectroscopy (PAS) (MTEC, model 300) was used to identify the nature of the surface functional groups of the aerosol particles deposited on the filter support.

## *Results*

DMA results (fig. 4) indicate that the SOA metrology depends on the molecular gas residence time  $\tau$  in the flow cell. At  $\tau = 1 \text{ min}$  the size distribution exhibits two modes, located at 60 and 180 nm. At  $\tau = 2 \text{ min}$  the size distribution consists of a single peak centered at 250 nm. During the SOA formation, we simultaneously follow the decay of the toluene signal (fig. 5) by Mass Spectrometry (MS). The integral is compared to the mass of collected SOA on the filter and leads us to conclude that the SOA aerosol yield is lower than 10%. Finally, FTIR-PAS experiments (fig. 6) clearly show the presence of the O-H stretching vibration (large absorption between 2500 and 3650  $\text{cm}^{-1}$ ), the C-H stretching vibration (asymmetric and symmetric, respectively, at 2920 and 2850  $\text{cm}^{-1}$ ) and the carbonyl band at 1720  $\text{cm}^{-1}$ .

Since FTIR-PAS is not a quantitative technique for the measurement of the number of functional groups, we have chosen a **titration technique** using a gas-phase probe molecule undergoing a **heterogeneous chemical reaction**. For that purpose we have used a Knudsen cell low pressure flow reactor (fig. 7) with probe molecules whose nature determines the surface functional groups to be examined. In order to detect the quantity of oxidizable sites we have used oxidizing molecules such as O<sub>3</sub> or NO<sub>2</sub>, for the acidic sites the base N(CH<sub>3</sub>)<sub>3</sub>, and for the detection of surface carbonyl groups NH<sub>2</sub>OH has been used.

The use of the Knudsen cell flow reactor is a good method for establishing the total number of molecules lost from the gas phase because of adsorption and/or reaction. The principle of our method is illustrated in figure 8 for the reaction of O<sub>3</sub> on a toluene soot substrate. The blue curve displays the ozone MS signal at  $m/e = 48$  which represents the rate of effusion of surviving gas phase O<sub>3</sub> molecules. During reaction the time integration of the hatched area of the curve displayed in figure 8 directly obtains the number of O<sub>3</sub> molecules lost from the gas phase. This value corresponds to the number of oxidizable sites of our sample calculated per mass unit ( $2.0 \cdot 10^{17}$  sites/mg). Using the other probe molecules we have performed similar titration experiments whose results are summarized in the following table.

	O <sub>3</sub>		NO <sub>2</sub>		(CH <sub>3</sub> ) <sub>3</sub> N		NH <sub>2</sub> OH	
	# / mg	product	# / mg	product	# / mg	product	# / mg	product
SOA	-	-	No reactivity	-	$1.3 \cdot 10^{15}$	salt	$\cong 1 \cdot 10^{16}$	oxime
soot	$2.0 \cdot 10^{17}$	O <sub>2</sub>	$1.8 \cdot 10^{16}$	HONO	$4.0 \cdot 10^{15}$	salt	$\cong 1 \cdot 10^{16}$	oxime

In contrast to soot, SOA aerosols do not interact with NO<sub>2</sub>. We neither observed uptake of NO<sub>2</sub> nor formation of HONO. Therefore, SOA particles are probably not responsible for the formation of HONO in the troposphere. The soot interface contains about four times more acidic sites than the SOA interface. Finally, preliminary results indicate that both soot and SOA substrates contain a large quantity of carbonyl groups ( $\cong 1 \cdot 10^{16}$  sites/mg).

### Conclusion

**The heterogeneous titration** is an appropriate technique to measure the nature and the number of surface functional groups. It allows us to characterize with great accuracy the gas-condensed phase interface by gas-phase probes rather than by chemical examination of the bulk of the particles. This study is fundamental because the functional groups distributed on the surface determine particle reactivity towards atmospheric gases. It is the first stage necessary to understand the chemical mechanisms of transformation in the atmosphere and their consequence for the radiative forcing of these aerosol particles.

### Acknowledgment

Generous support of Office Fédéral de l'Enseignement et de la Science (OFES) is gratefully acknowledged in the framework of the EU projects NITROCAT and THALOS.



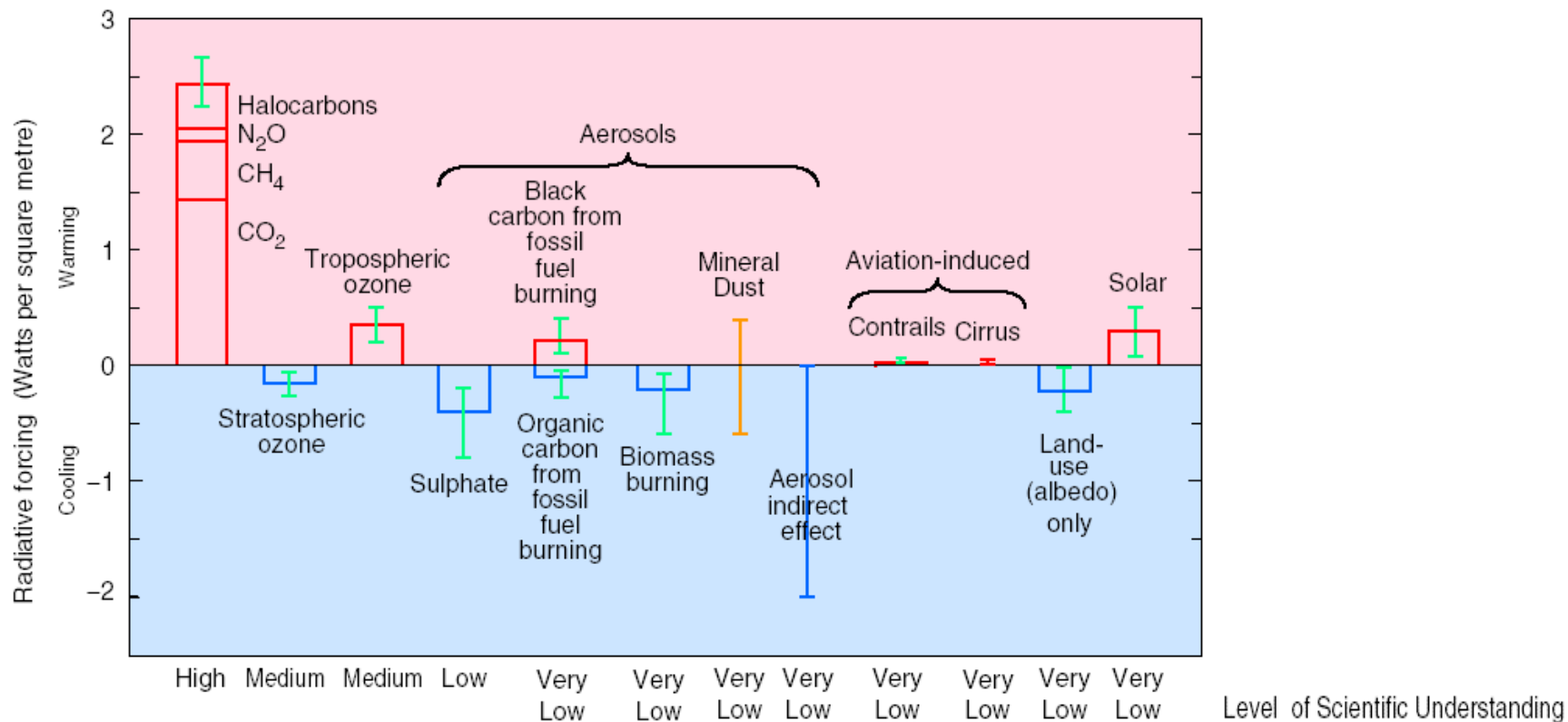
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Chemical reactivity of soot and Secondary Organic Aerosols  
generated under laboratory conditions

# Scientific Goal: Impact of Aerosols on radiative Forcing

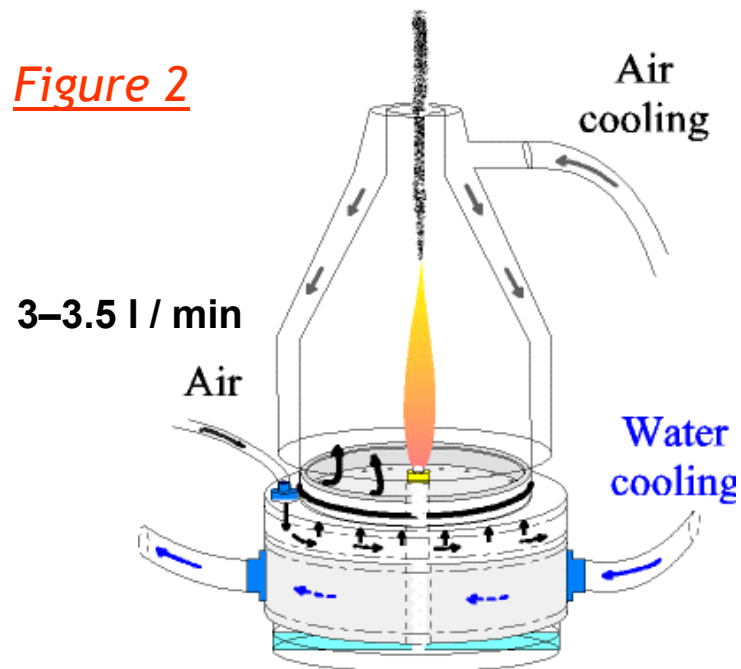
- Large uncertainties on the effect of aerosols on radiative Forcing, very low level of scientific understanding

**Figure 1**



- “The radiative forcing due to aerosols depends not only on these spatial distributions, but also on the size, shape, and chemical composition of the particles ...” (IPCC, 2001)
- Toluene is the most abundant aromatic compound in urban air ( $\cong 6\%$  of the observed non methane hc)

**Figure 2**



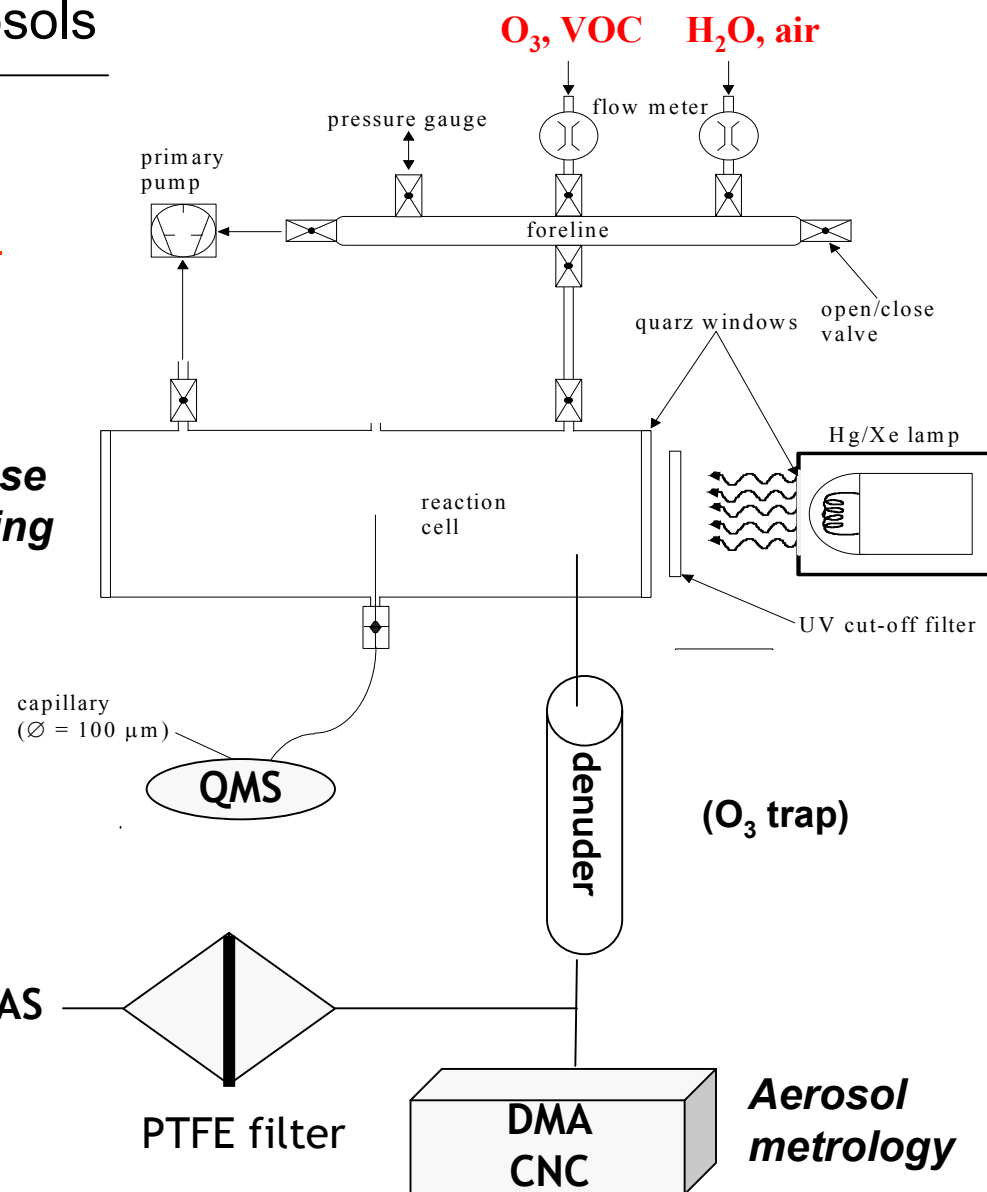
- Burner used to produce soot from liquid toluene (rich flame)
- High production rate ( $\cong$  mg / min)

SOOT:

**Combustion of toluene**

**Figure 3**

**Gas phase monitoring**



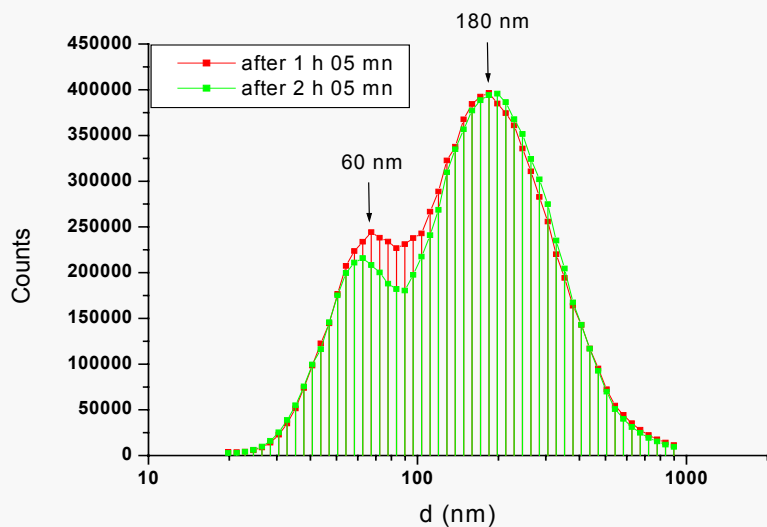
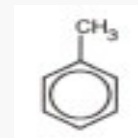
SOA:

**Photooxydation of toluene**

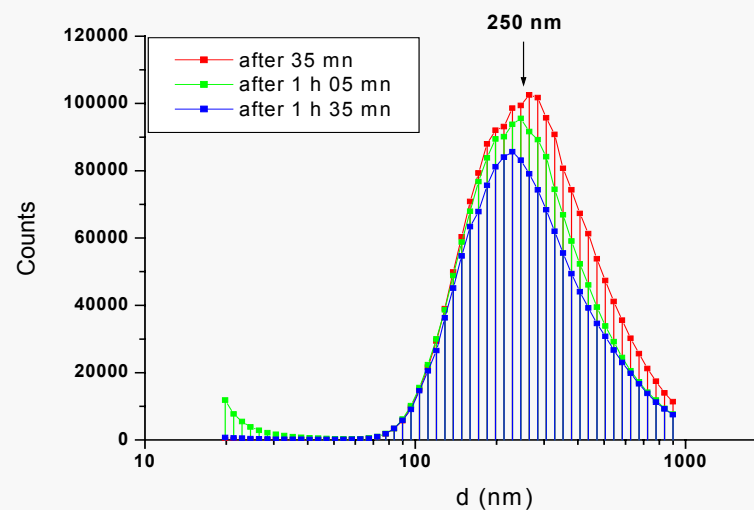
*Figure 4*

Residence time $\tau$ (min)	Total conc. part / cm <sup>3</sup>	Total vol. conc. nm <sup>3</sup> / cm <sup>3</sup>
1	6.3 10 <sup>6</sup>	9.8 10 <sup>13</sup>
2	1.1 10 <sup>6</sup>	6.7 10 <sup>13</sup>

**Metrology vs gas residence time  $\tau$**

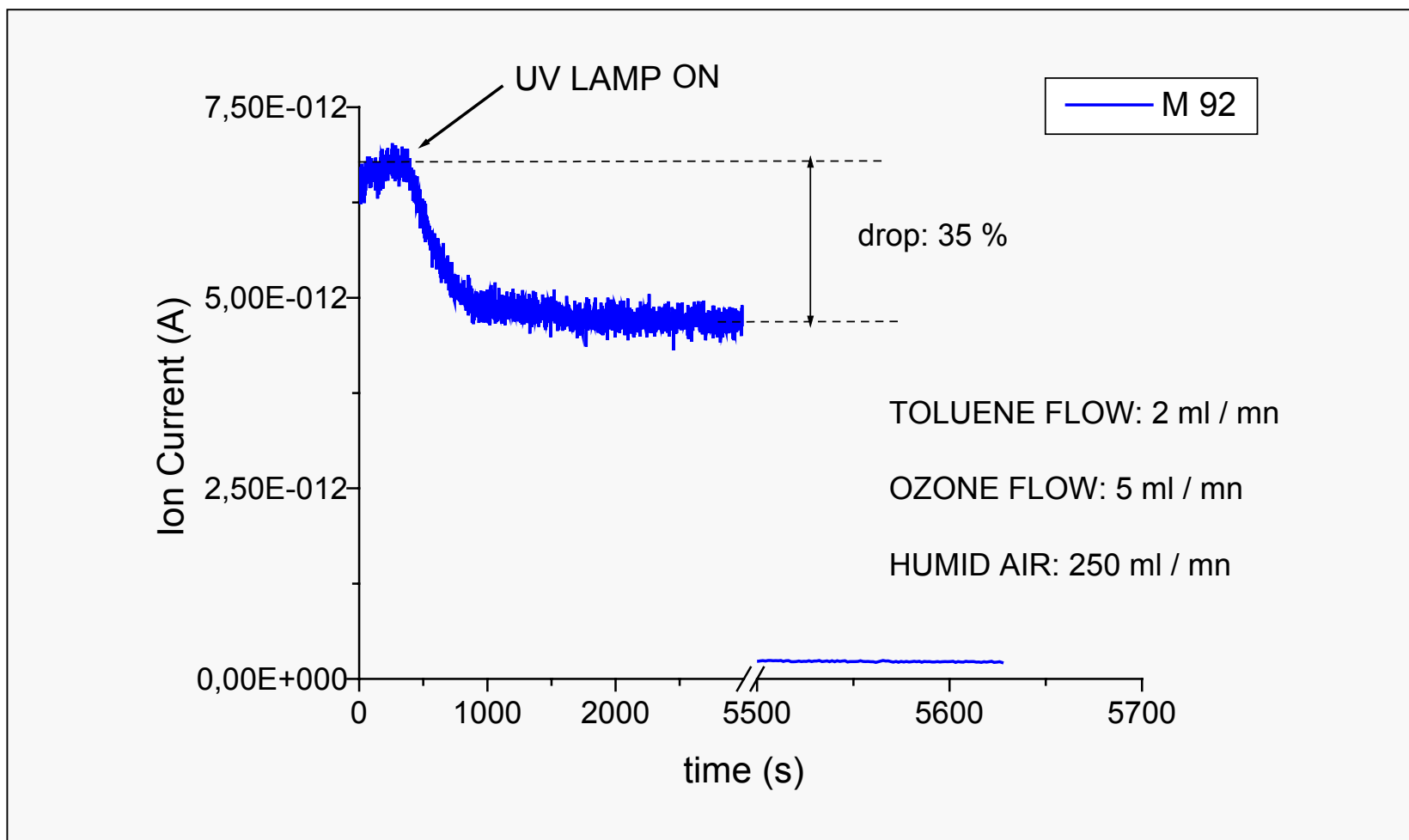


$\tau = 1 \text{ min}$

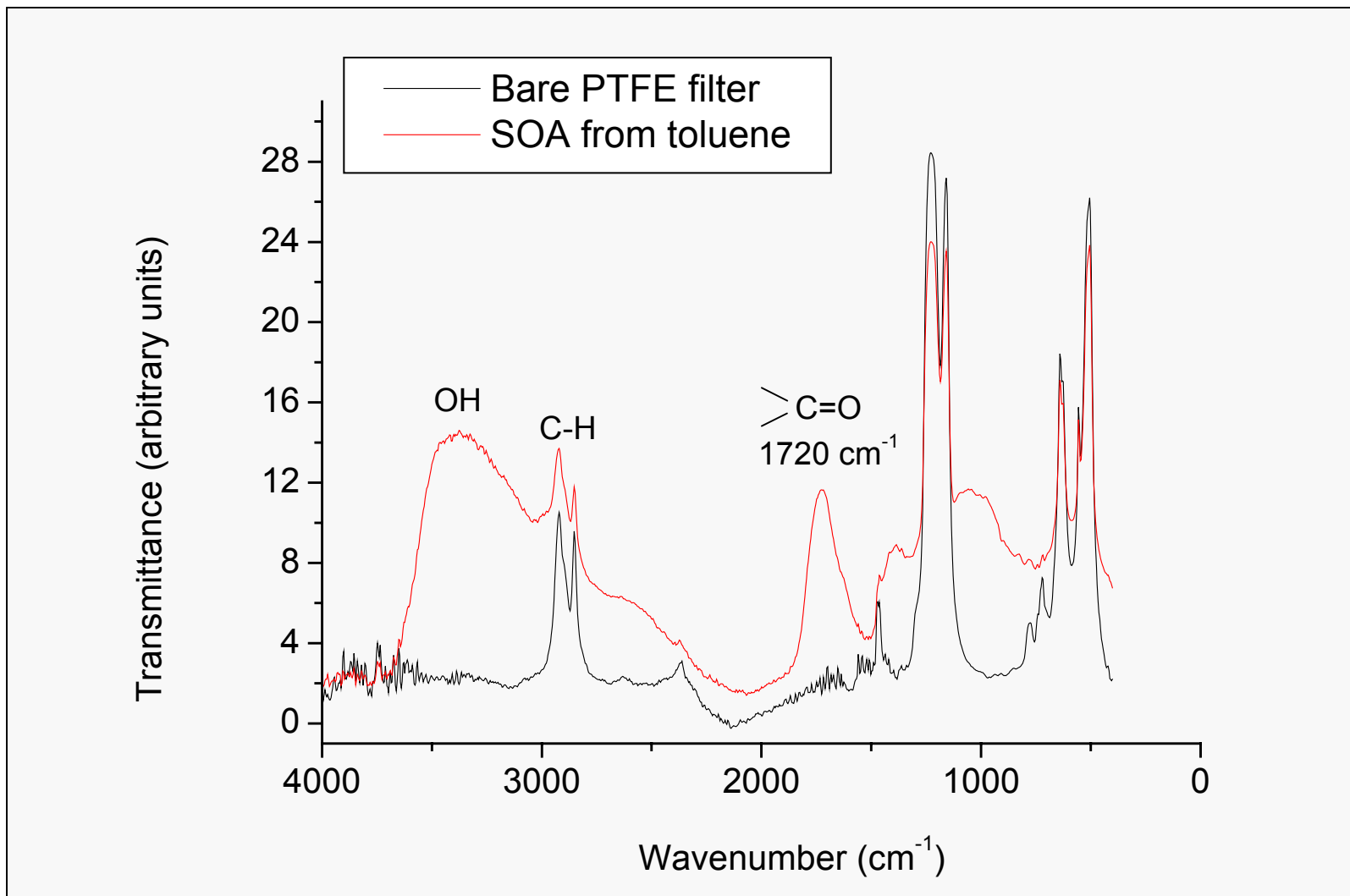


$\tau = 2 \text{ min}$

Figure 5



Simultaneous monitoring of toluene in the gas phase and the mass of the collected SOA leads to an aerosol yield < 10 %



**Figure 6:** FTIR-PAS leads to identification of surface functional groups

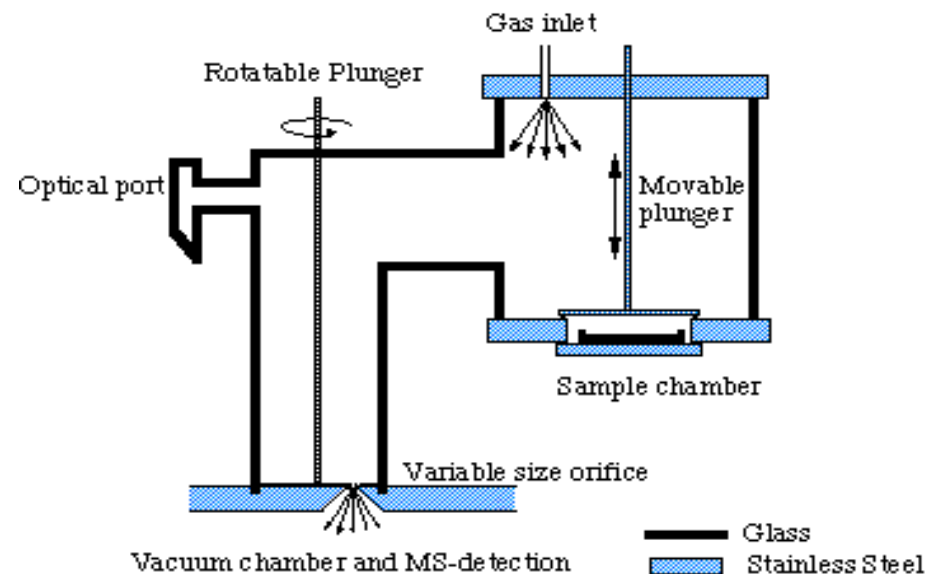


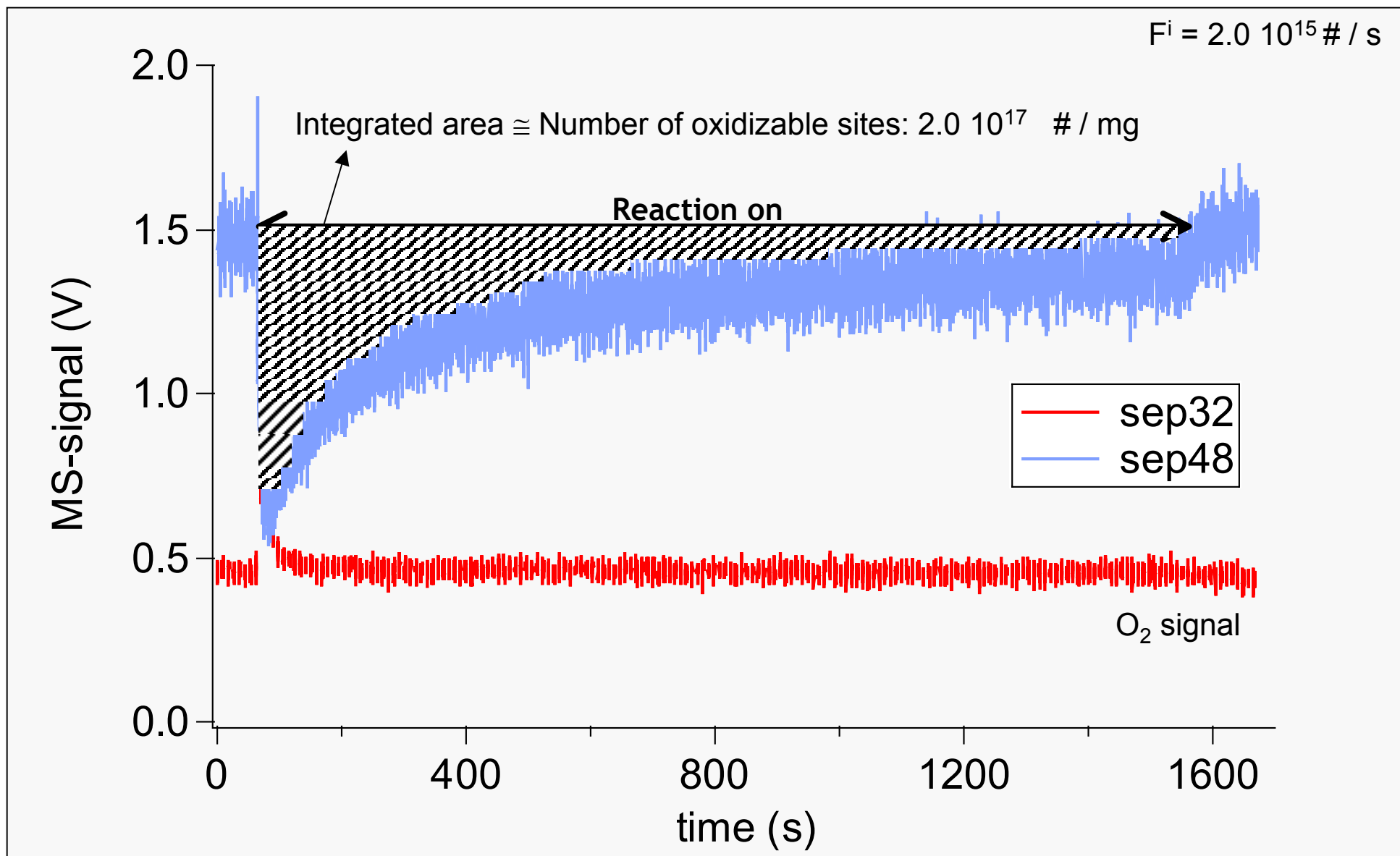
- ❑ FTIR-PAS is not a quantitative technique to measure the number of functional groups
  
- ❑ Chemical identification using a **titration technique** with a gas-phase probe molecule in a **heterogeneous chemical reaction**
  - Knudsen cell low pressure flow reactor
  
  - The nature of the probe molecules determines the surface functional groups to be examined
    - $O_3$ ,  $NO_2$        $\dashrightarrow$       oxidizable sites
    - Base                     $\dashrightarrow$       acidic sites
    - $NH_2OH$                $\dashrightarrow$        $>C=O$  containing sites

# Knudsen cell: a low pressure flow Reactor

*Figure 7*

- ❑ Flowing gas experiment
- ❑ Relative rate technique, upon lifting the plunger effusing molecules compete with reaction/adsorption on reactive surface
- ❑ Kinetics are presented in terms of uptake (sticking) coefficients
- ❑ Method for establishing the total number of lost molecules during the gas phase residence time





□ NO<sub>2</sub> / SOA (Toluene)

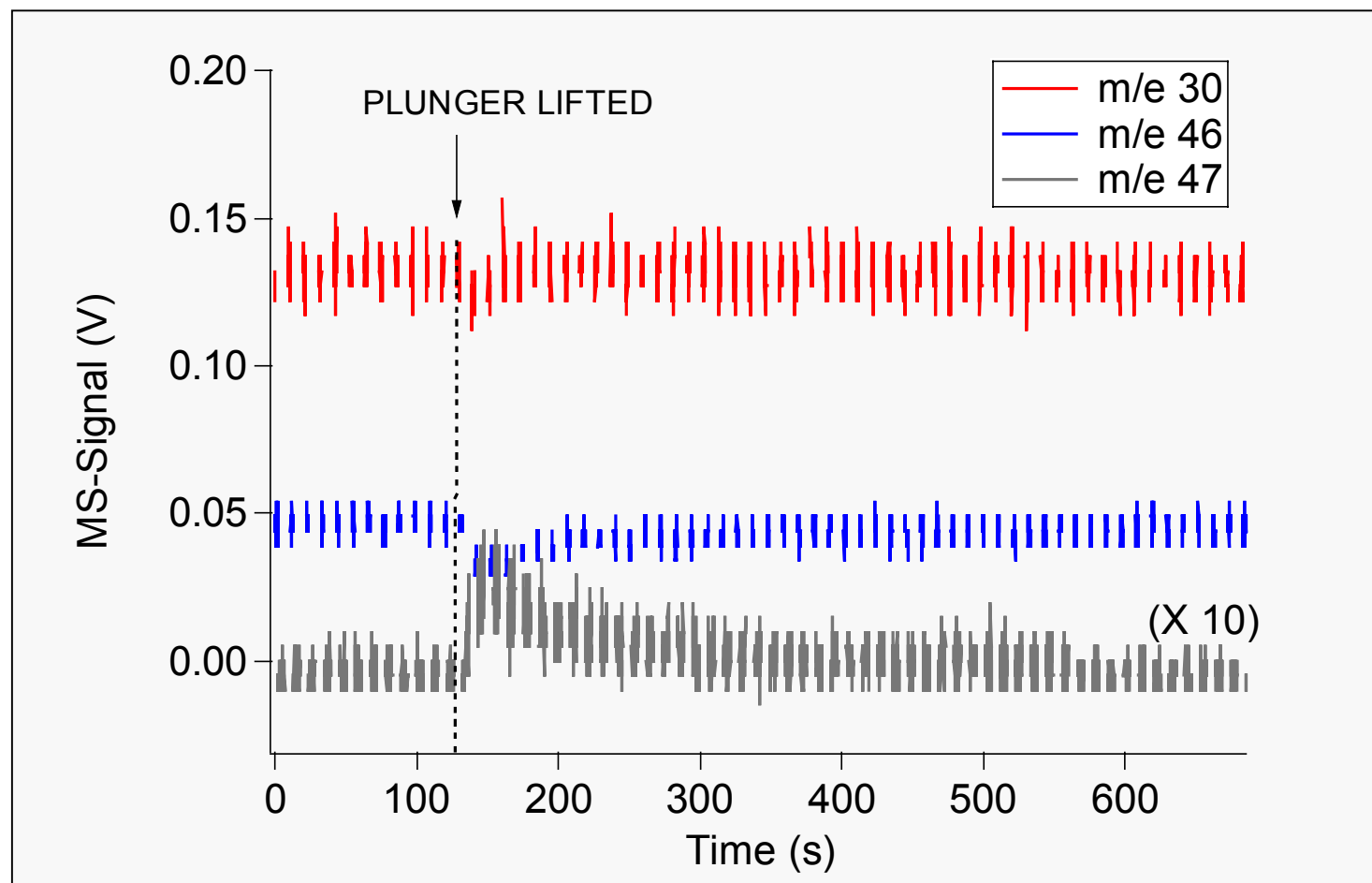
***no reactivity, SOA is not responsible for the formation of HONO in the atmosphere***

□ NO<sub>2</sub> / SOOT (Toluene)

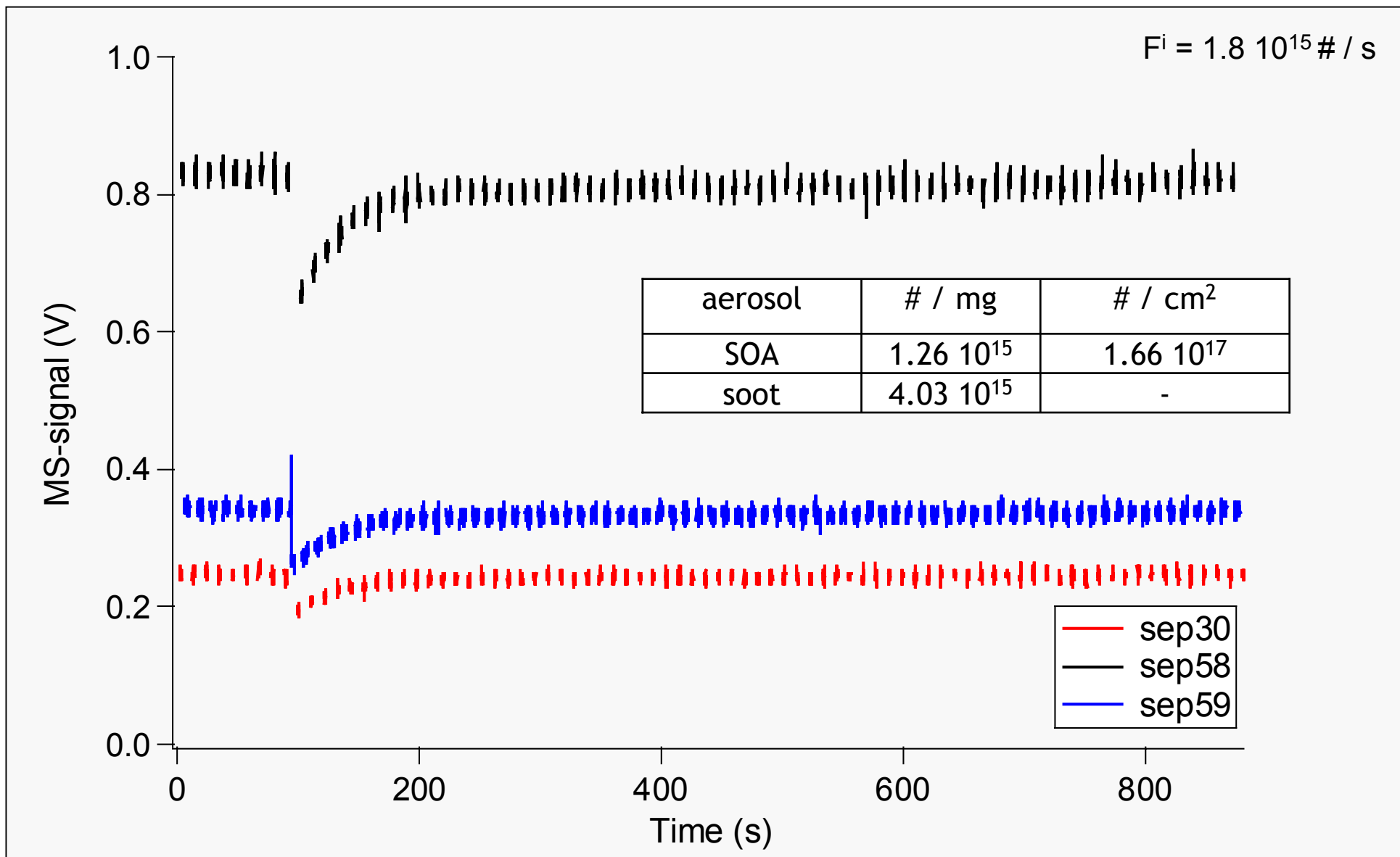
• NO<sub>2</sub> uptake :

➤  $1.81 \cdot 10^{16}$  # / mg

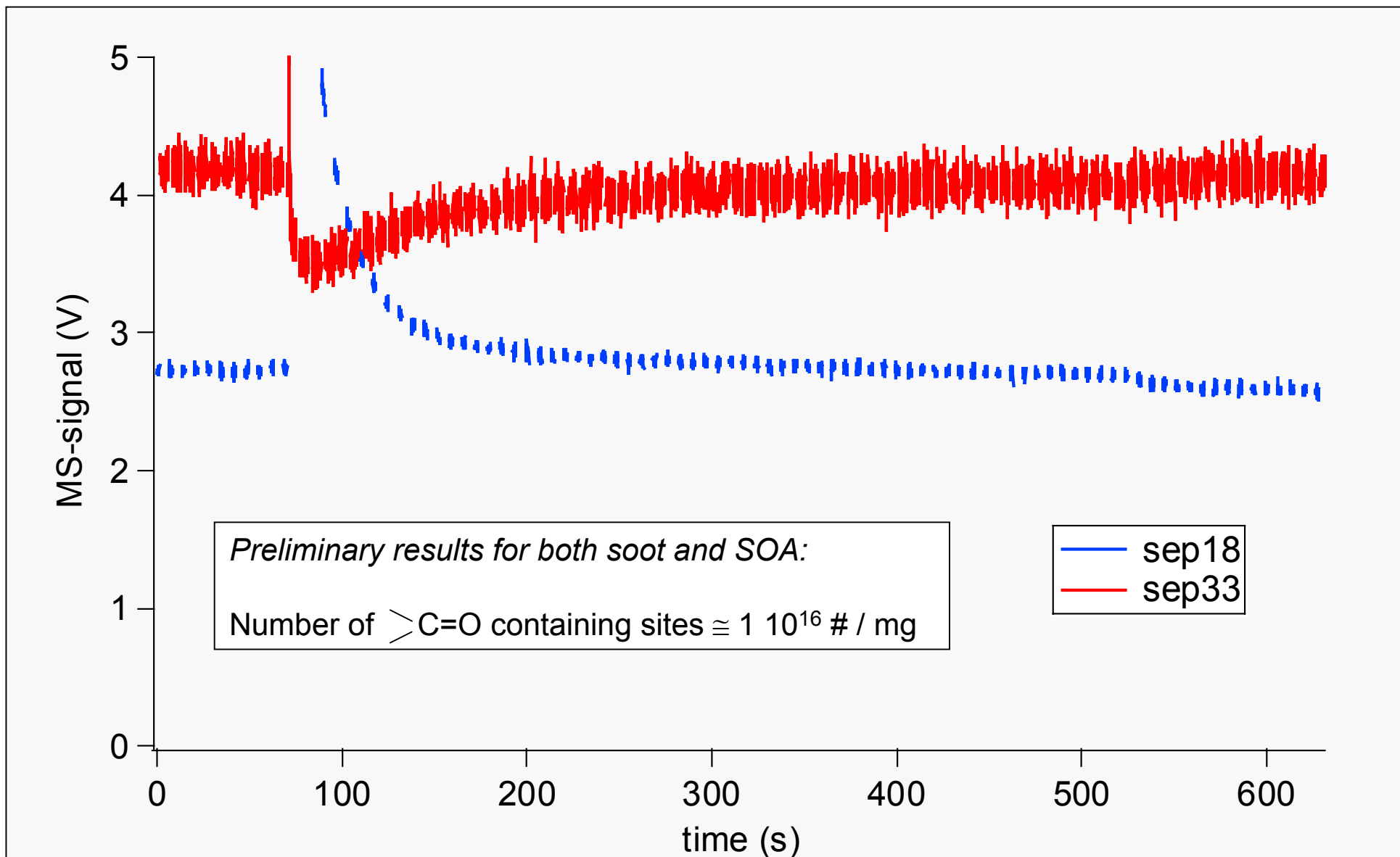
• HONO production



# (CH<sub>3</sub>)<sub>3</sub>N: probing the acidic Properties of the Aerosol Interface



# (NH<sub>2</sub>)OH: detection of sites containing C=O



## Conclusions

	O <sub>3</sub>		NO <sub>2</sub>		(CH <sub>3</sub> ) <sub>3</sub> N		NH <sub>2</sub> OH	
	# / mg	product	# / mg	product	# / mg	product	# / mg	product
SOA	-	-	No uptake	-	1.3 10 <sup>15</sup>	salt	≅ 1 10 <sup>16</sup>	oxime
soot	2.0 10 <sup>17</sup>	O <sub>2</sub>	1.8 10 <sup>16</sup>	HONO	4.0 10 <sup>15</sup>	salt	≅ 1 10 <sup>16</sup>	oxime

- The **heterogeneous titration** is an appropriate technique to measure the nature and the number of surface functional groups that are “visible” from the gas phase
- Strong reactivity of O<sub>3</sub> on the soot surface (interest for atmospheric chemistry)
- In contrast to soot, SOA does not interact with NO<sub>2</sub>
- Soot interface contains four times more acidic sites than SOA interface
- Both soot and SOA interfaces contain a large quantity of carbonyl groups

