Field Measurement of Nanoparticle Surface Area using the Geometric Surface Area Monitor by the Weighted Sum Method

Leo Cao and David Y.H. Pui

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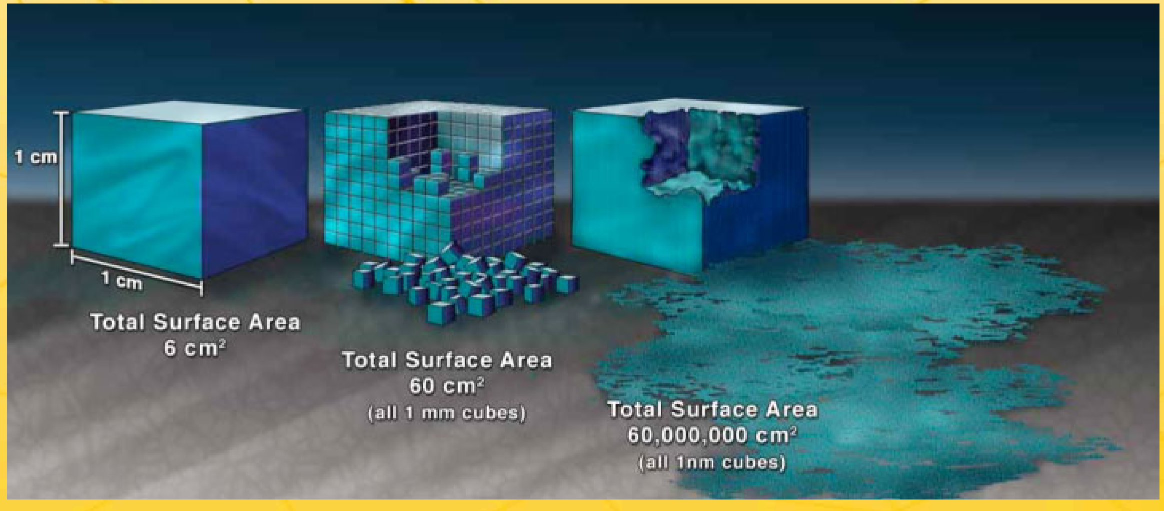
Outline

- Background and objective
- Methodology
- Experiments
- Summary

Significance of surface area



- Catalytic activity
- Drug delivery
- Particle reactivity
- Health effect

1 → 10,000,000x surface area

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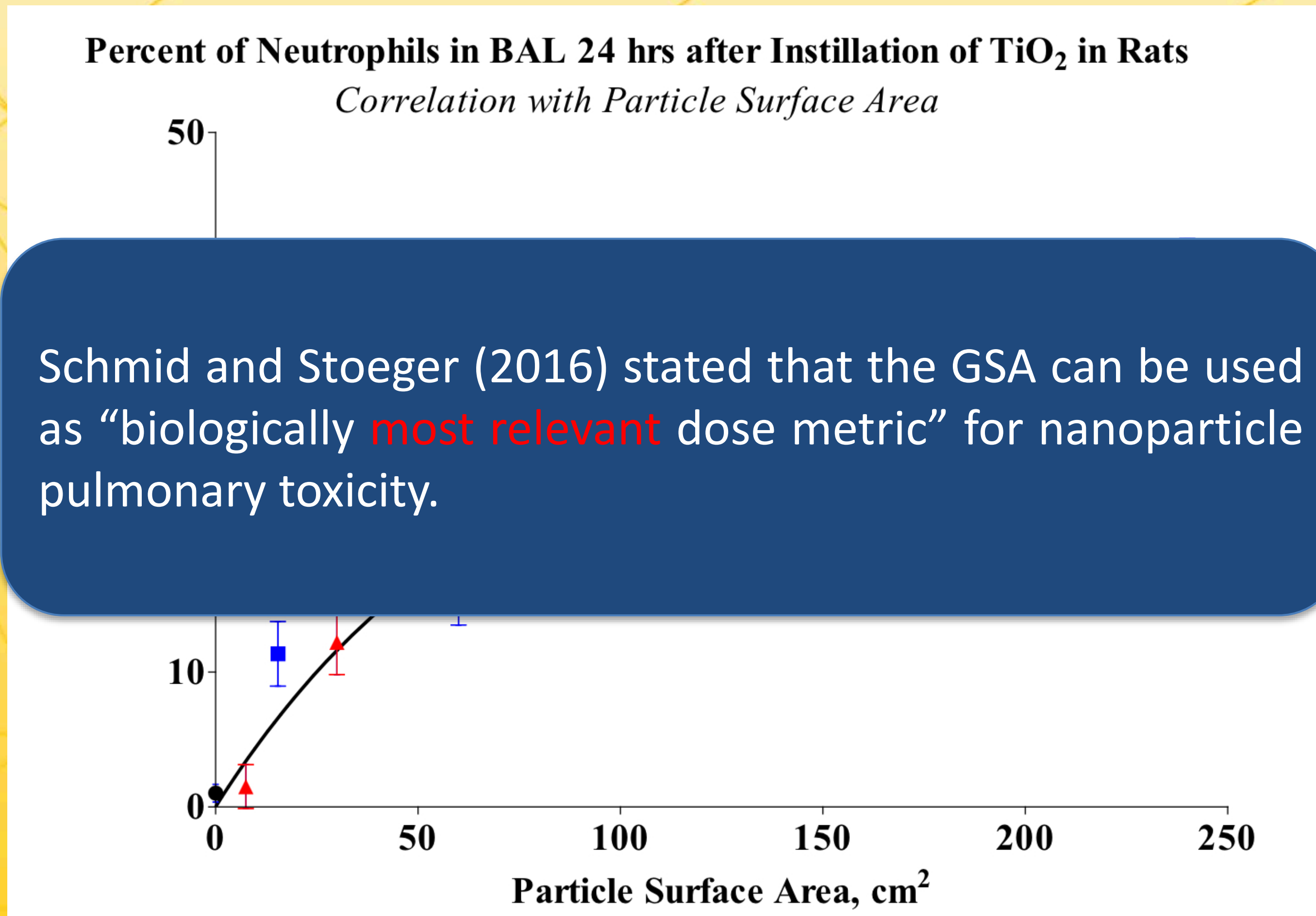
Health effect



Schmid and Stoeger (2016) stated that the GSA can be used as “biologically most relevant dose metric” for nanoparticle pulmonary toxicity.

Oberdörster, G. (2000). Pulmonary effects of inhaled ultrafine particles. *International archives of occupational and environmental health, 74*(1), 1-8.

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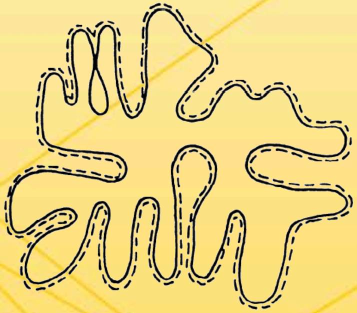
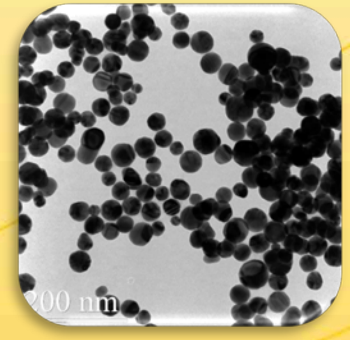
Methods for surface area: offline



BET method (gas adsorption):

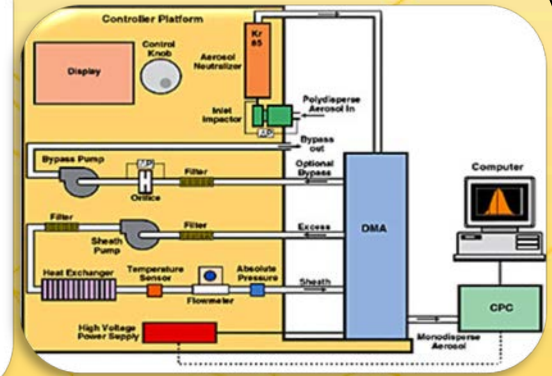
- Surface area including pores
- Direct (standard)
- Ex situ
- Time consuming
- Costly



Electron microscopy (TEM and SEM):

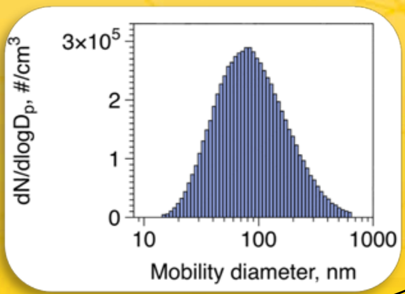
- 2D projected area
- Ex situ
- Time consuming
- Costly

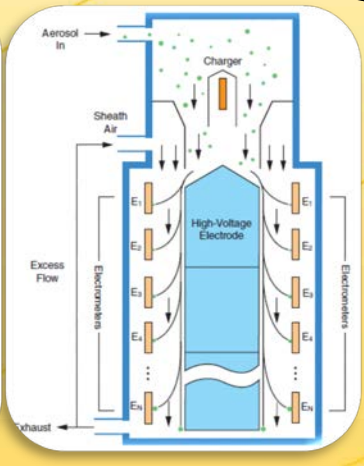
Methods for surface area: online



Scanning Mobility Particle Sizer (SMPS)
Spectrometer:

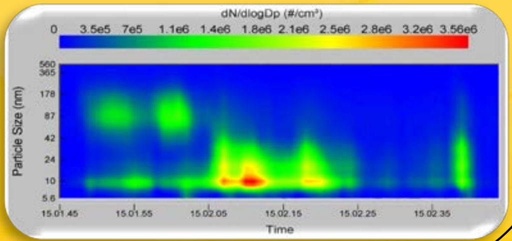
- Mobility diameter based distribution
- Minutes
- Bulky
- Working fluid
- Radiation source
- Costly



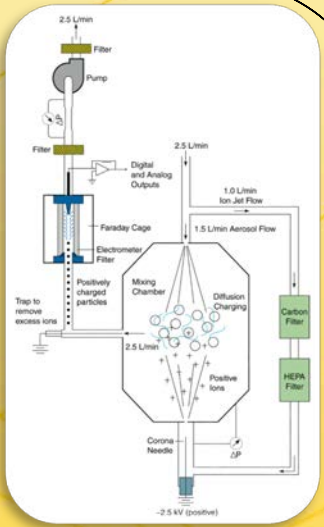


Fast Mobility Particle Sizer (FMPS)
Spectrometer:

- Mobility diameter based distribution
- 1 s resolution
- Bulky
- Data inversion
- Costly

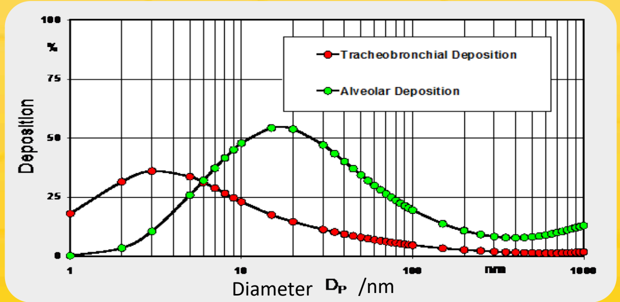


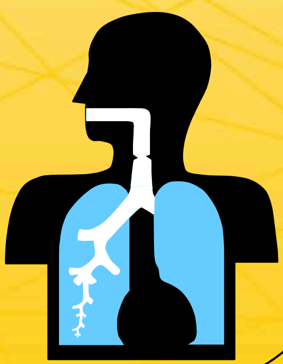
Methods for surface area: online 2



Nanoparticle Surface Area Monitor (NSAM)*:

- Mobility diameter based
- 1 s resolution
- Reasonable size and cost for field measurement
- Only lung-deposited surface area





One step further, Cao and Pui et al., (2017)# developed a Geometric Surface Area Monitor based on this. However, it needs an additional ESP and inertial impactor, which cause pressure drop and measuring range problem.

So far, no quick and easy way to measure the geometric surface area (GSA) of particles

#Cao, L. N. Y., Chen, S.-C., Fissan, H., Asbach, C., & Pui, D. Y. H. (2017). Development of a geometric surface area monitor (GSAM) for aerosol nanoparticles. Journal of Aerosol Science, 114, 118-129. doi:https://doi.org/10.1016/j.jaerosci.2017.09.013

*Fissan, H., Neumann, S., Trampe, A., Pui, D. Y. H., & Shin, W. G. (2007). Rationale and principle of an instrument measuring lung deposited nanoparticle surface area. *Journal of Nanoparticle Research, 9*(1), 53-59. doi:10.1007/s11051-006-9156-8

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Objective

A cost effective method delivering geometric surface area (GSA) concentration of nanoparticles in real time.

Features:

- Real time, GSA
- No working fluid, no radiation source, no significant pressure drop, and large range.

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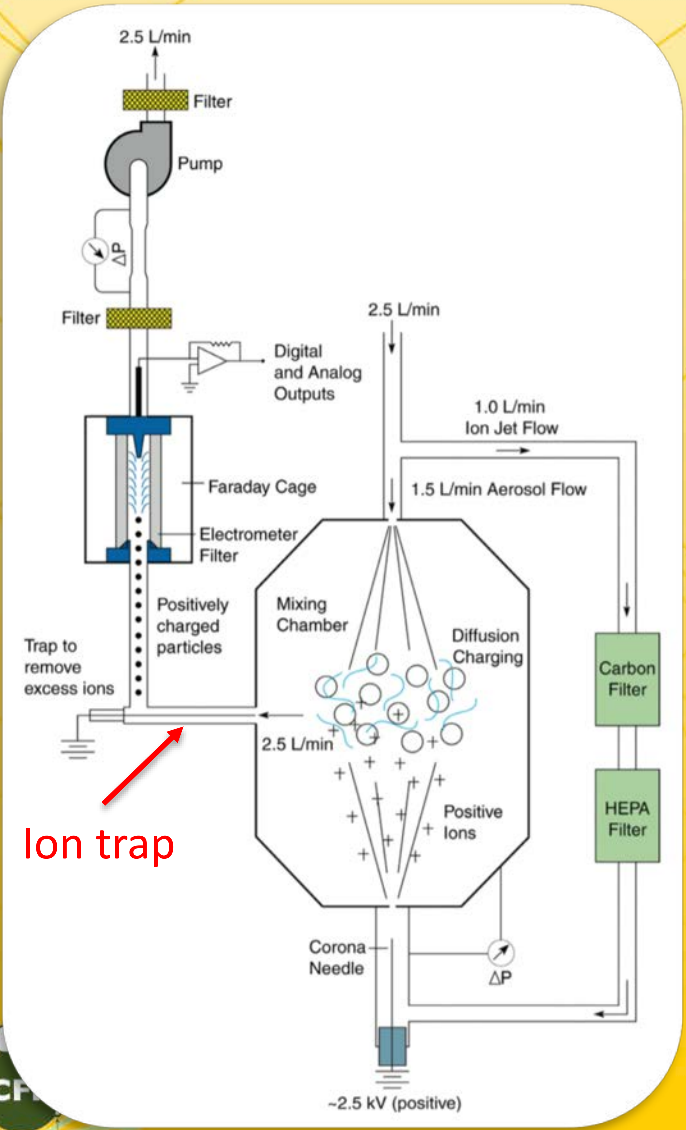
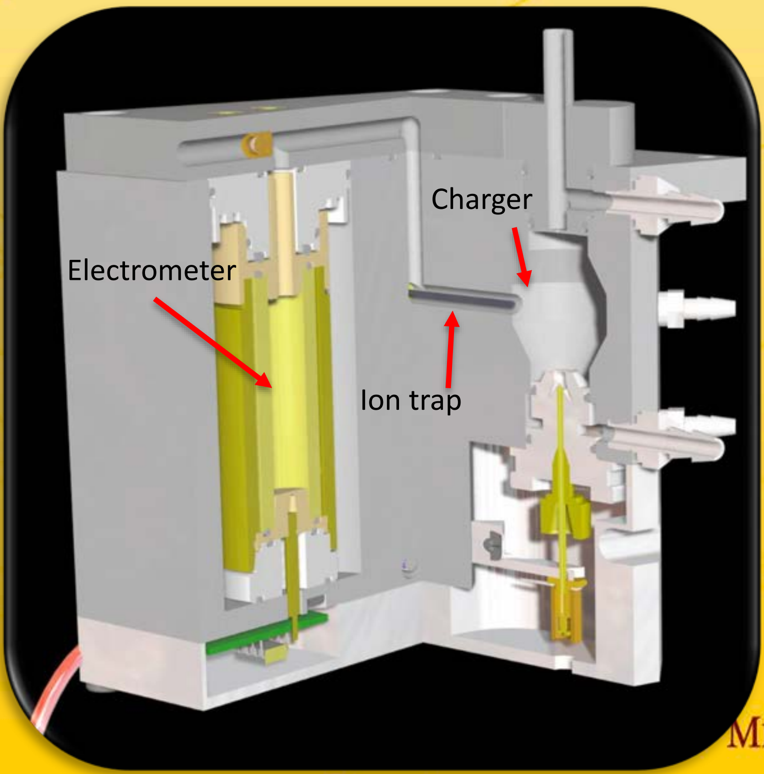
Methodology

- Using Nanoparticle Surface Area Monitor (NSAM) as the basic tool and no additional devices

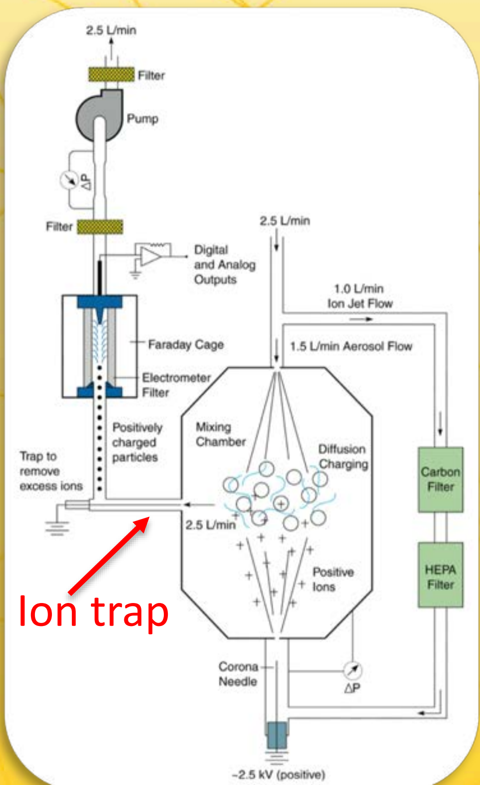
- Linearly combining the signal (under different conditions) to fit GSA (geometric surface area) measurement.

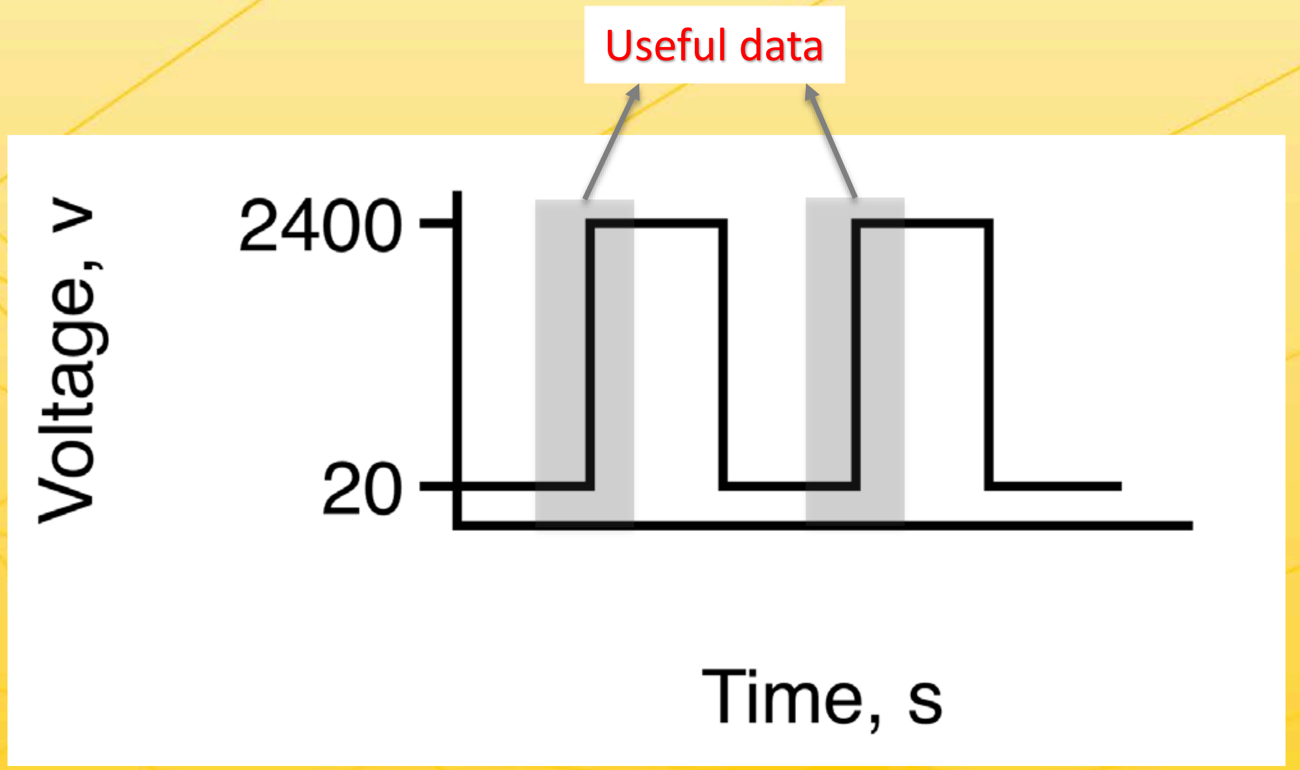
NSAM
(Nanoparticle Surface Area Monitor)





Geometric Surface Area Monitor (GSAM): block-shaped voltage pulse



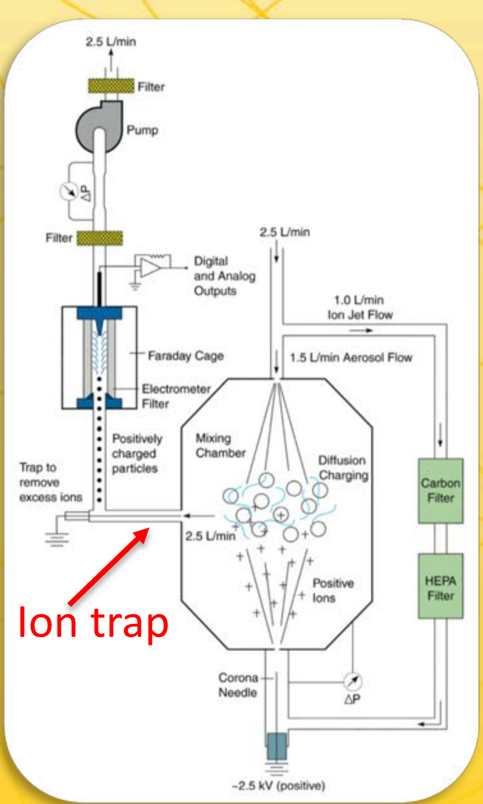


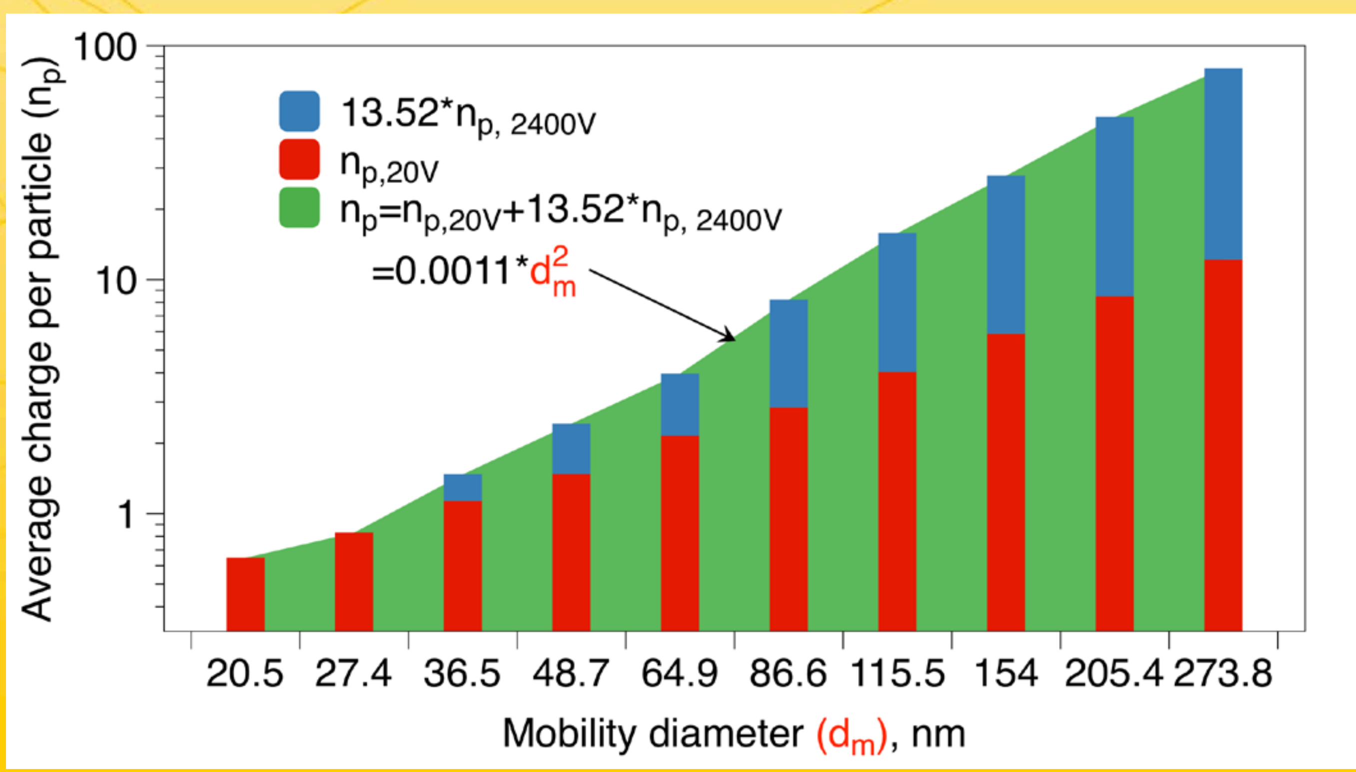
LabVIEW-controlled voltage pulse makes the continuous sampling.

Changing voltage of ion trap

Combining instrument responses under different voltages

Average charge of particle ∝ surface area





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Field measurement

- Parallel sampling using GSAM and SMPS
- Location or event:

Lab 4130: 5 hours

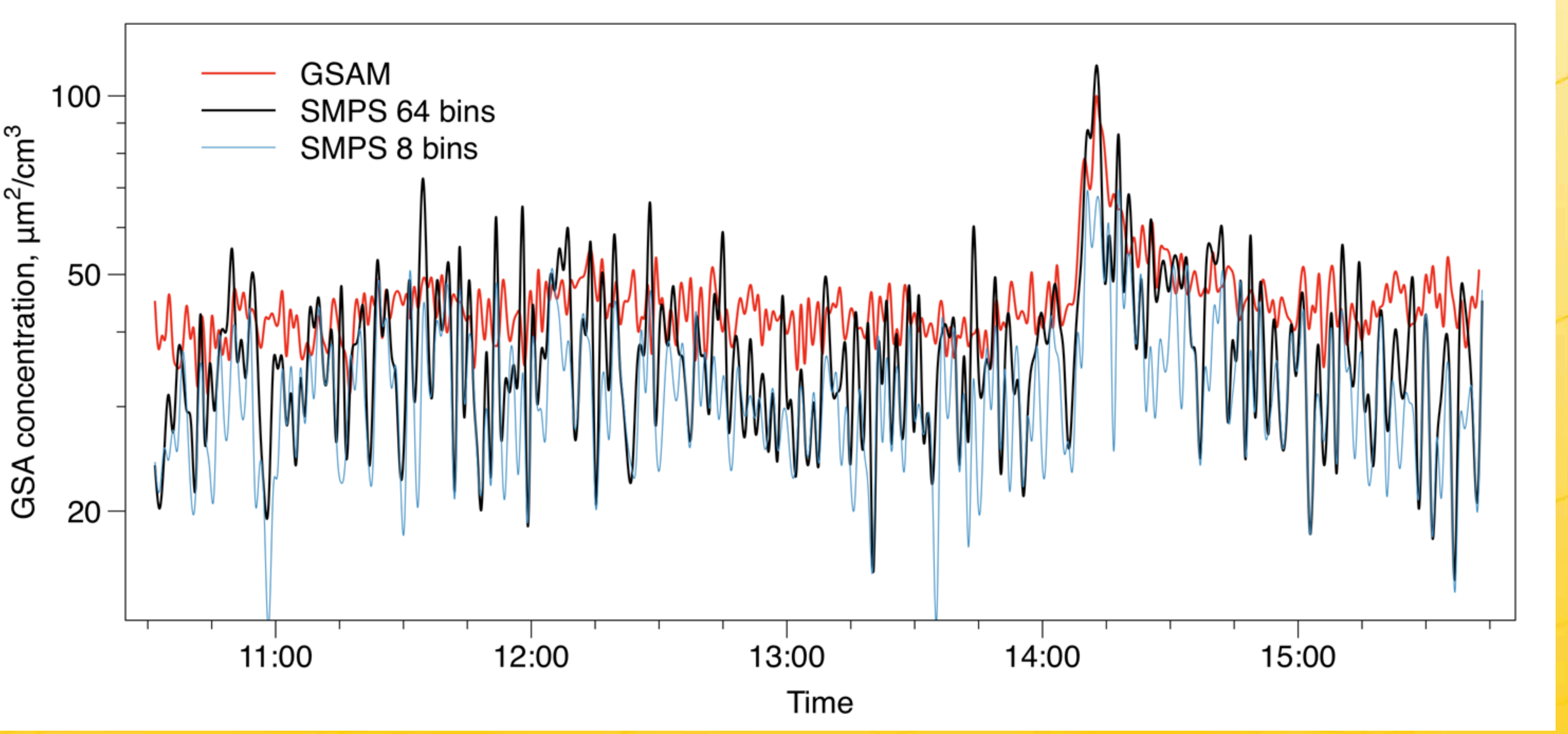
Outdoor: 5 days

laser printing: 1 hour

3D printing: 8 hours

Lab ME4130

Sampling length: ~5 hours



- At very low concentration, the GSA from GSAM and SMPS agree well with each other including the emission event.
- GSAM is more stable.

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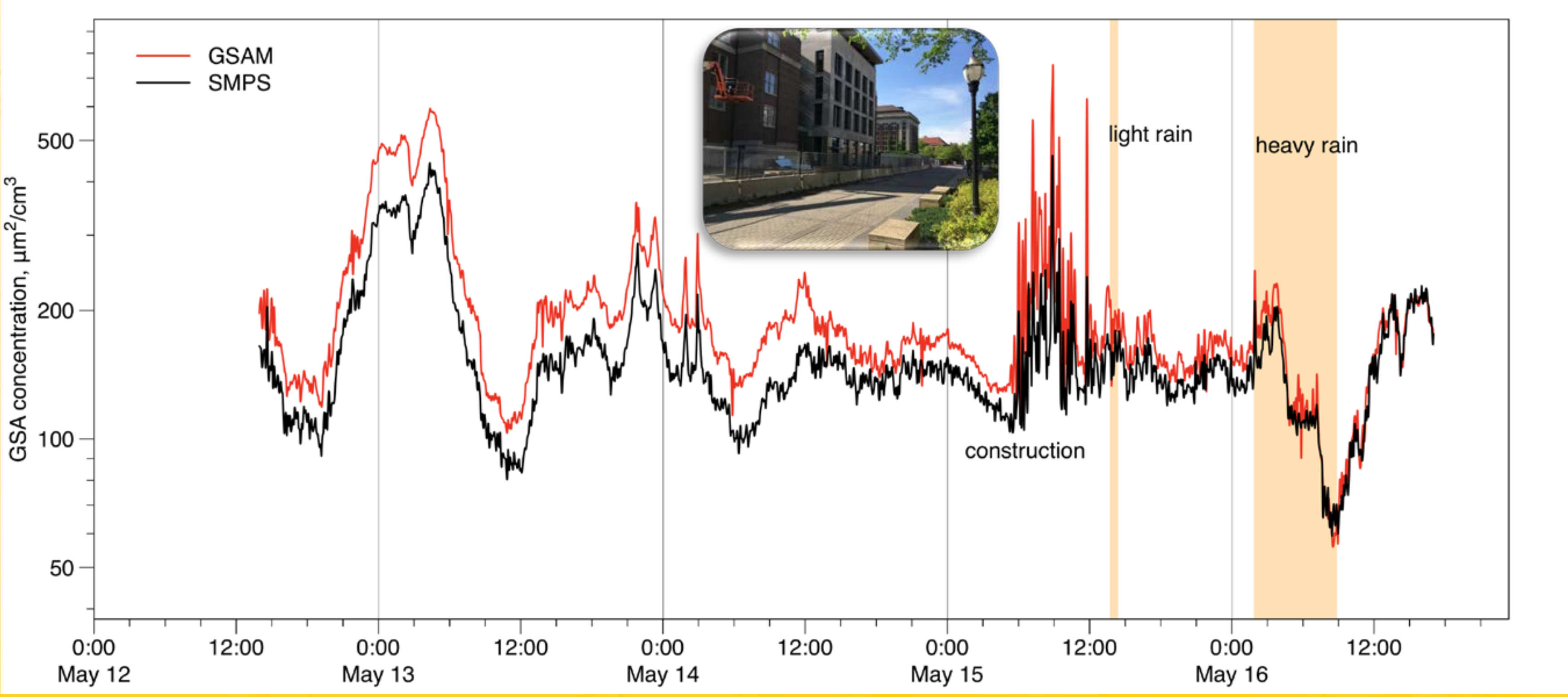
5 days outdoor sampling



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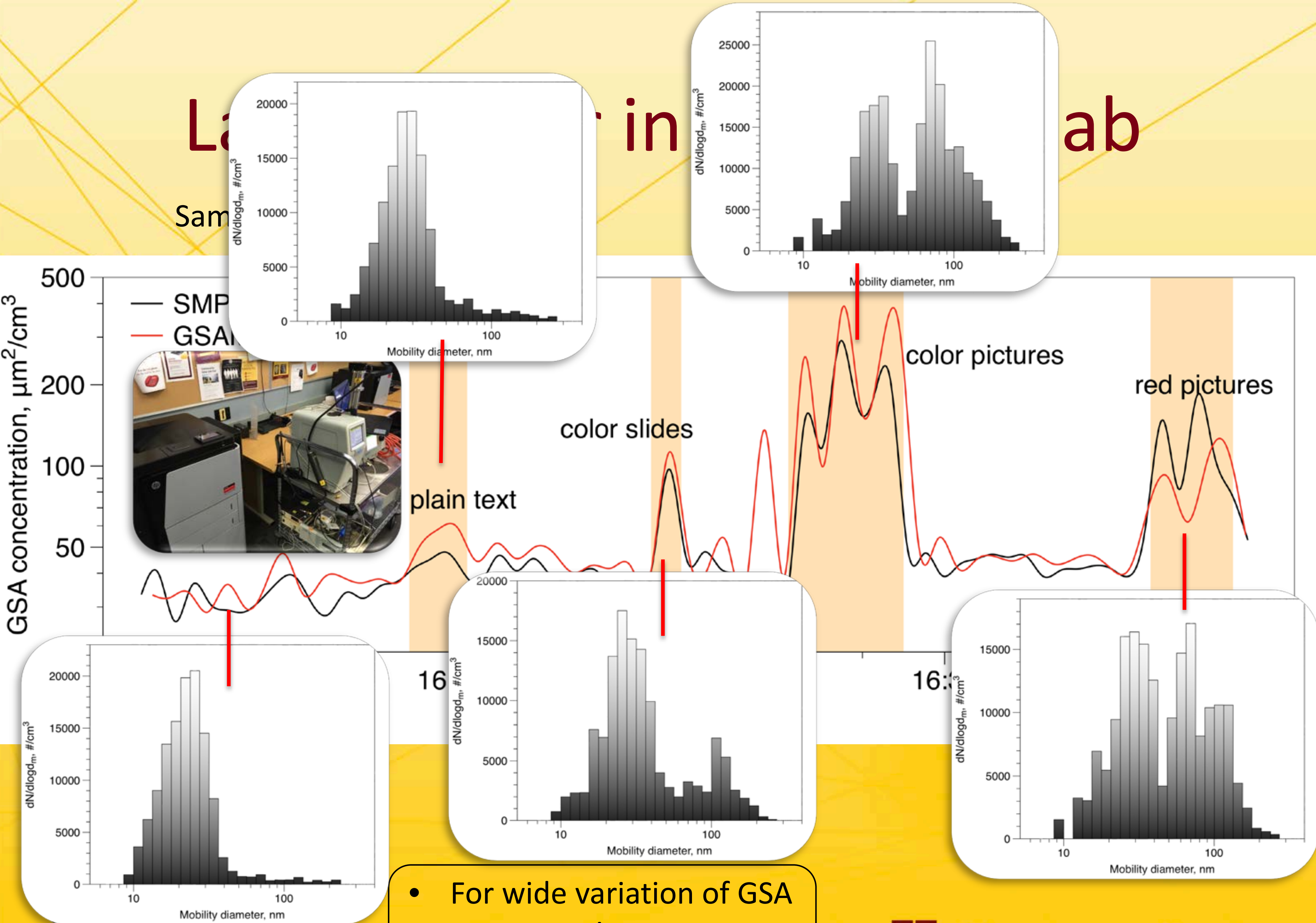


- For wide variation of GSA concentrations, two methods agree well.

3D printing

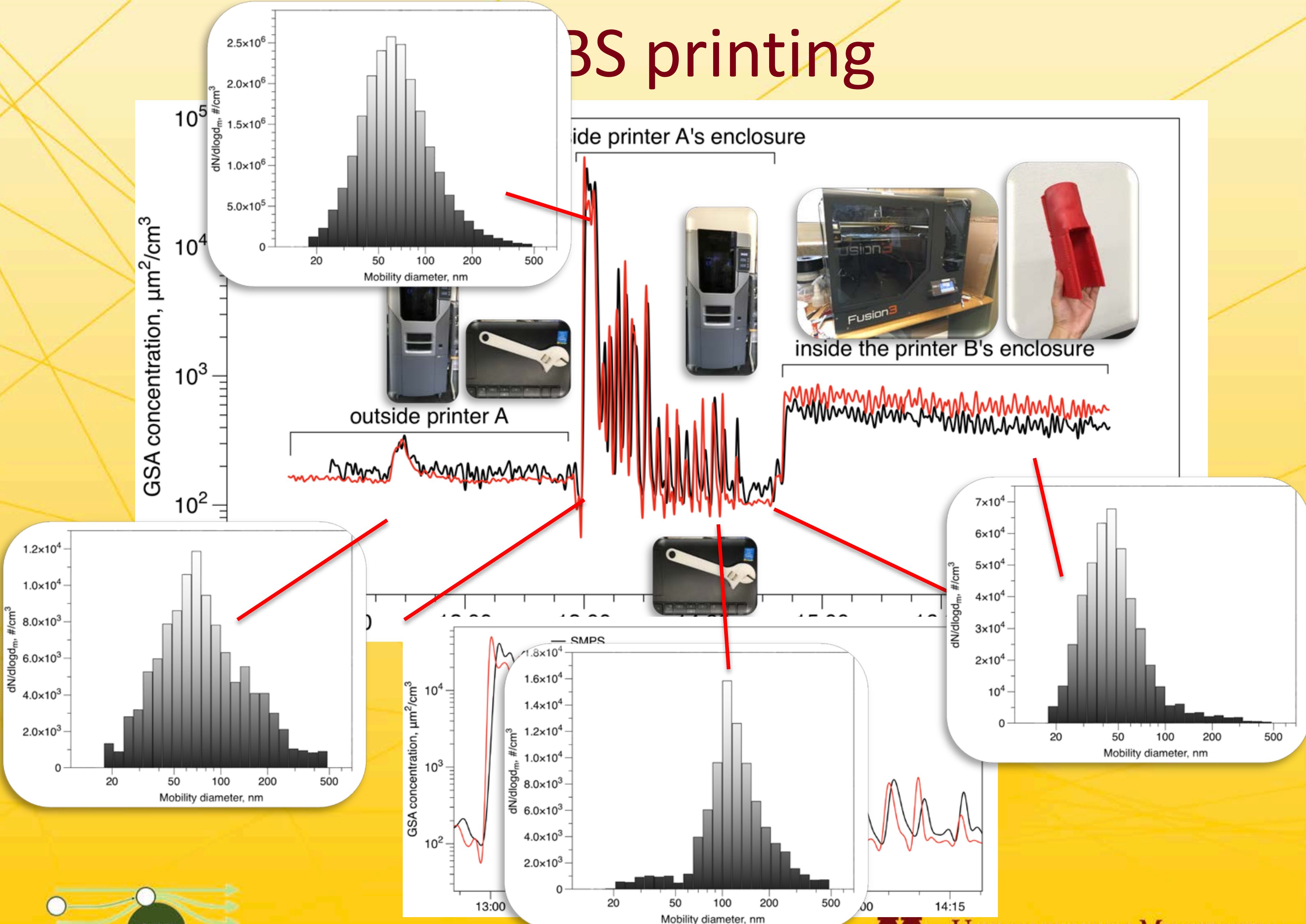
Printers: Dimension 1200es and Fusion3

Printing materials: **Acrylonitrile butadiene styrene (ABS)** and **Polylactic Acid (PLA)**

Material	Printing temperature	Decomposition temperature
ABS	230–250°C	380–430°C
PLA	200–235°C	300–400°C

X2

BS printing



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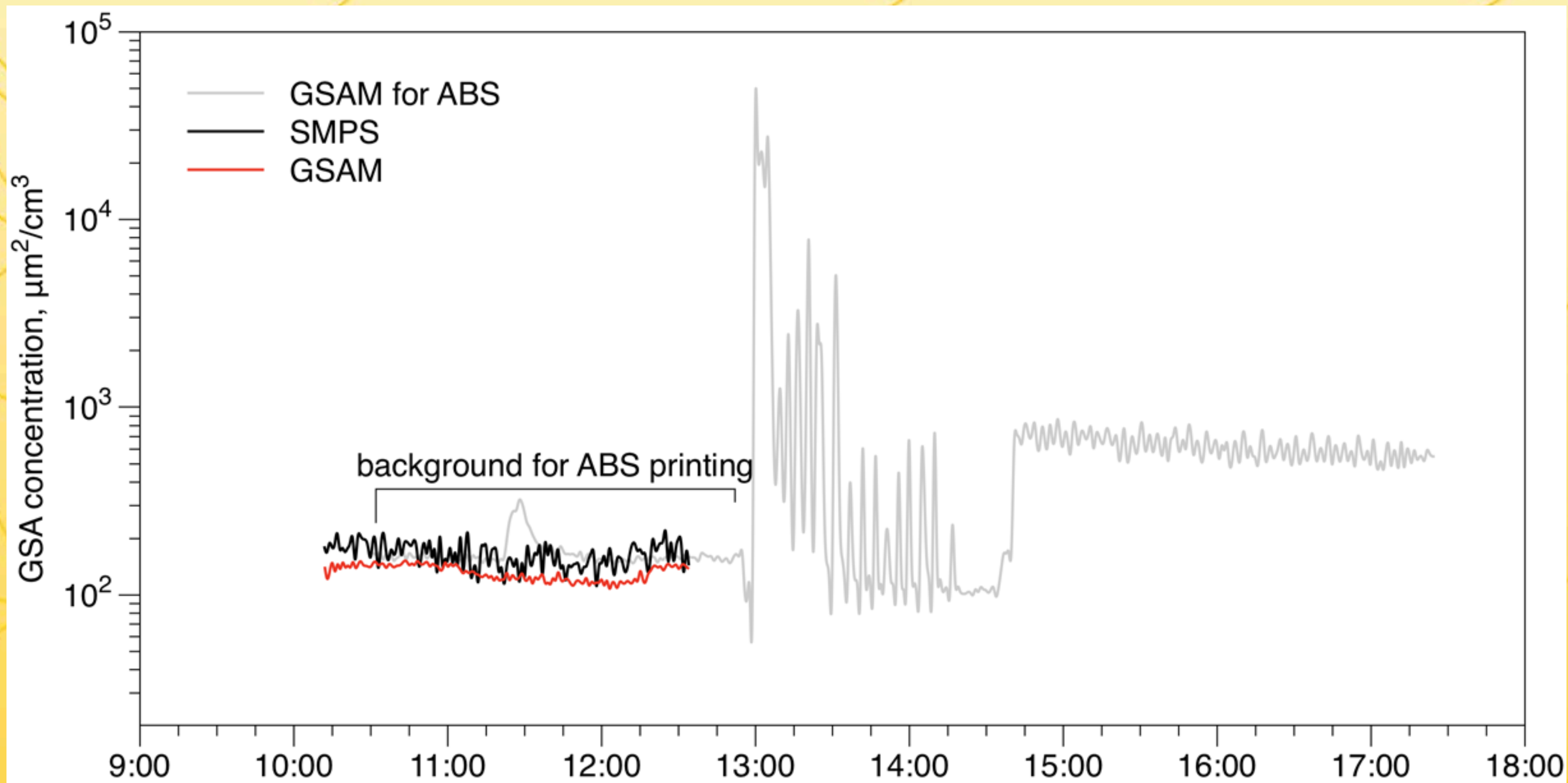
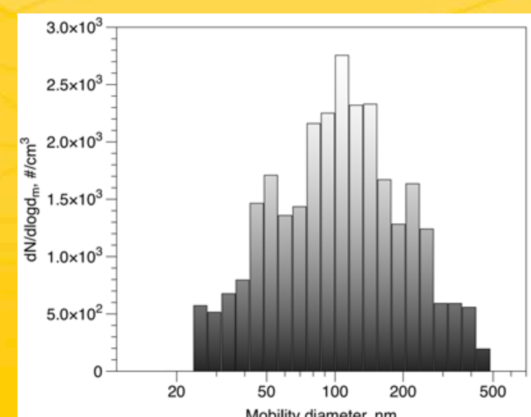
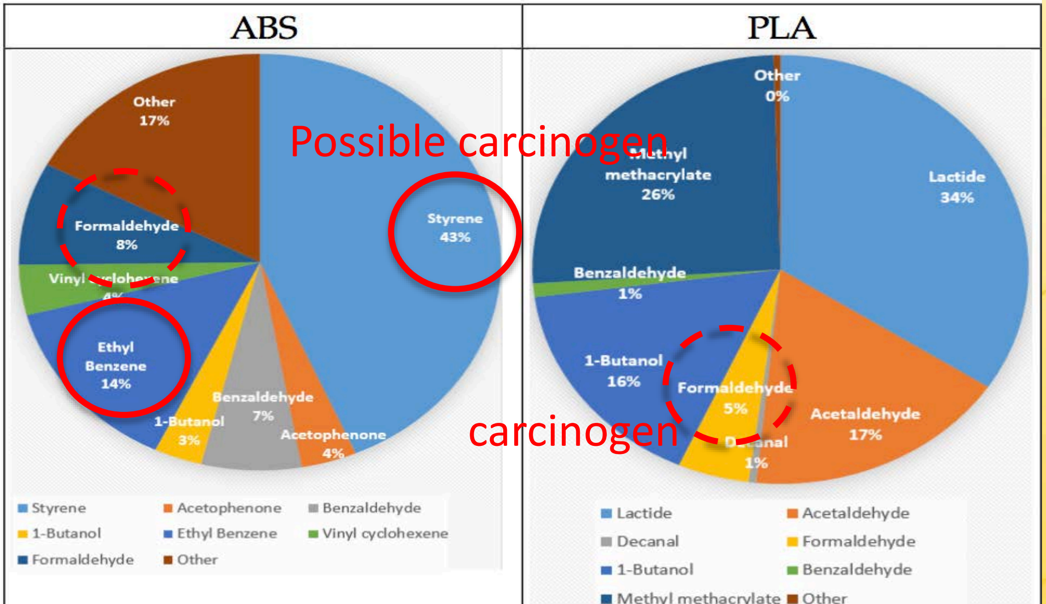
PLA printing



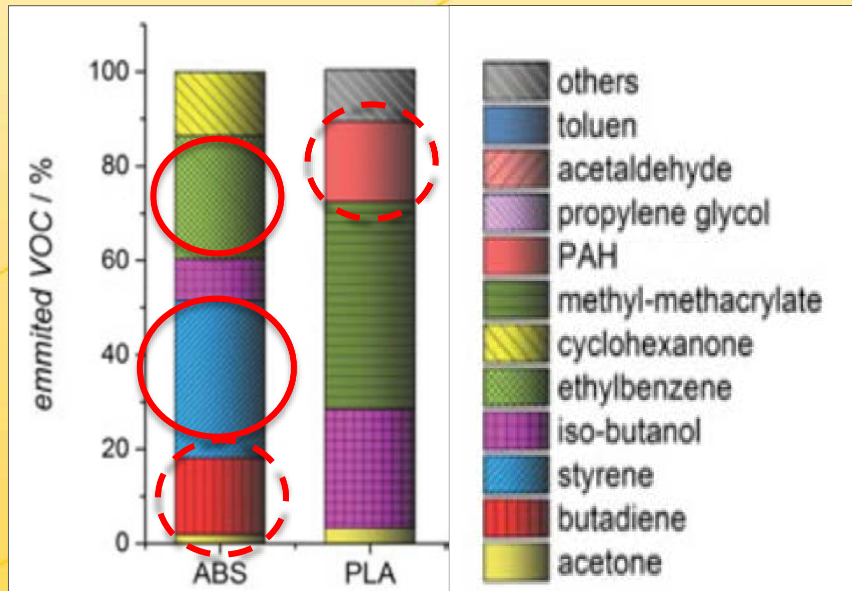


Comparison between ABS and PLA

- ABS printing has higher particle (also VOC) emission.



Davis, A. (2017).



Wojtyła et al., (2017).

- However, in the *in vitro*, *in vivo* and acellular assays tests, particle toxicity from PLA was "at the level of diesel vehicles", while that from ABS were much lower. (*Weber, 2017)*

Davis, A. (2017). VOC Emissions from FDMTM Desktop 3D Printers. Abstract retrieved from Abstracts in the safety science of 3D printing summit database.
Wojtyła, S., Klama, P., & Baran, T. (2017). Is 3D printing safe? Analysis of the thermal treatment of thermoplastics: ABS, PLA, PET, and nylon. Journal of Occupational and Environmental Hygiene, 14(6), D80-D85. doi:10.1080/15459624.2017.1285489
Weber, R. J. (2017). Fine Particulate Emissions from Desktop 3D Printers. Abstract retrieved from Abstracts in the safety science of 3D printing summit database.

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Filters of the printers

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Filters

HEPA filter

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Summary

The novel GSAM successfully measures the GSA of real-environment particles.

Printers should be carefully used and filters should be used to protect the users because of the emission during the printing.

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Thank you

Questions and/or comments
caoxx282@umn.edu

Appendix 1.1 Current, sensitivity, and GSA

$S(d, v_1, v_2, a) = S(d, v_1) + aS(d, v_2)$ (1)
If $S(d, v_1, v_2, a) = k\pi d^2$ (2)
where k is a constant that can be determined in the instrument calibration.

The total current measured by the electrometer for polydisperse aerosol can be expressed as:

$$I = I(v_1) + aI(v_2)$$
$$= \int_{d=0}^{+\infty} S(d, v_1) \frac{dN(d)}{dlogd} dlogd + \int_{d=0}^{+\infty} aS(d, v_2) \frac{dN(d)}{dlogd} dlogd$$
$$= \int_{d=0}^{+\infty} [S(d, v_1) + aS(d, v_2)] \frac{dN(d)}{dlogd} dlogd$$
$$= \int_{d=0}^{+\infty} S(d, v_1, v_2, a) \mathrm{d}N(d). \quad (3)$$

where *I(v)* is the total current measured by the electrometer.
Substituting Eq. 2 into Eq. 3,

$$I = k \int_{d=0}^{+\infty} \pi d^2 \mathrm{d}N(d) \quad (4)$$

where $\int_{d=0}^{+\infty} \pi d^2 \mathrm{d}N(d)$ is the total GSA concentration, A_g, in μm²/cm³ for the polydisperse aerosol, then

$$A_g = \frac{I}{k}. \quad (5)$$

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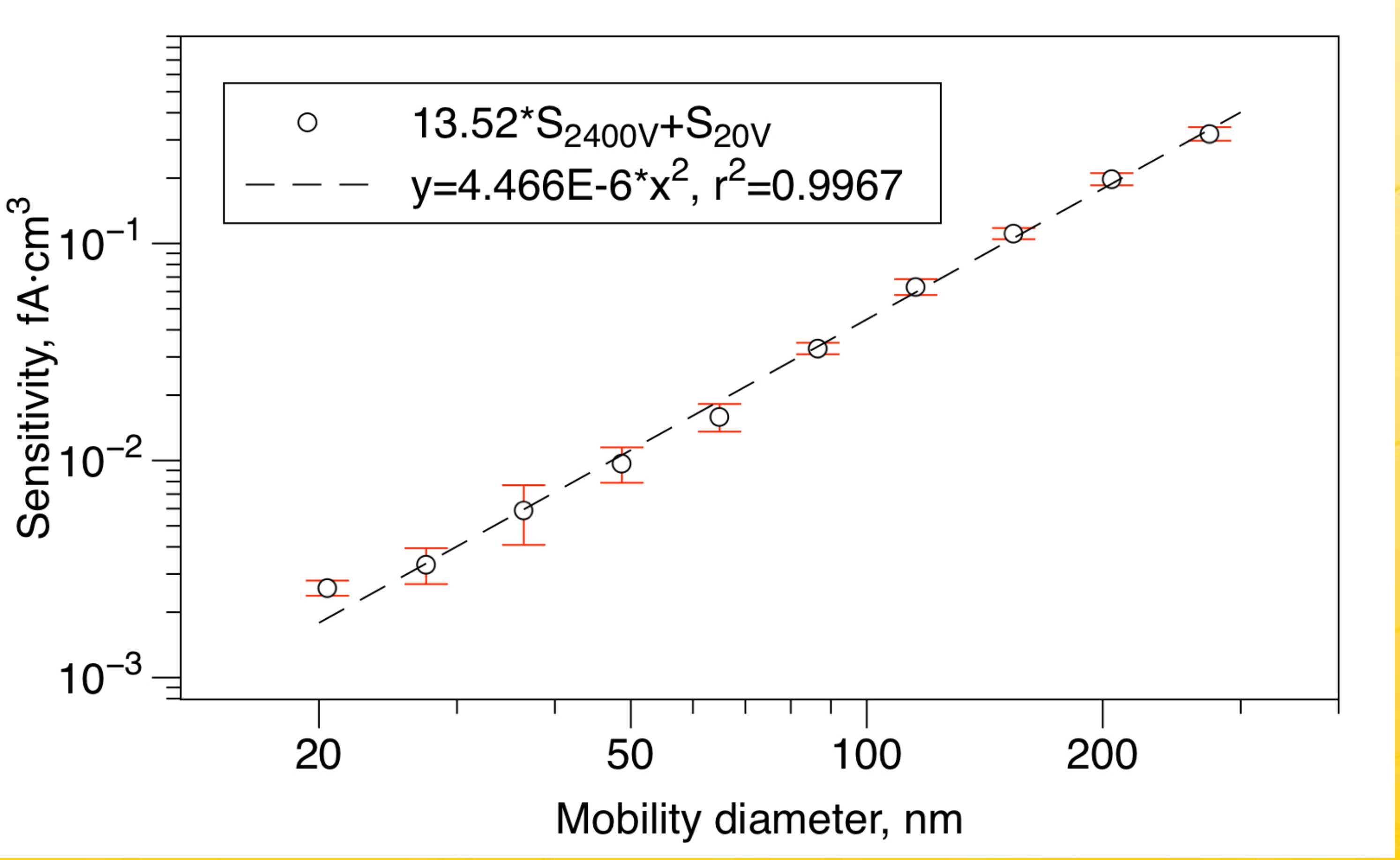
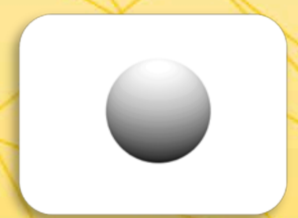
Appendix 1.2 Sensitivity fitting



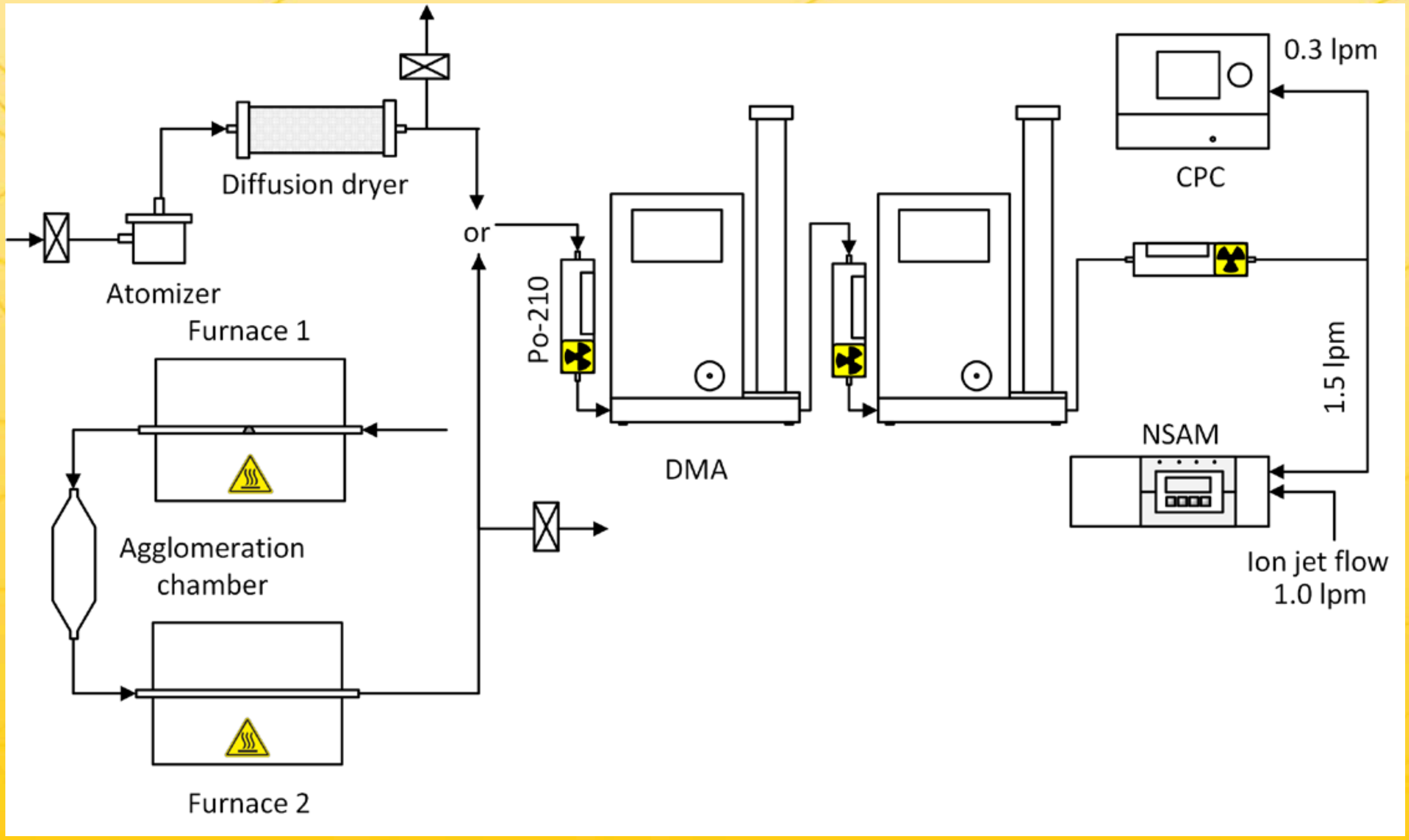
Appendix 2.1 Sensitivity of the monitor:

$$S = \frac{electrical\ current, fA}{number\ concentration, \#/cm^3}$$



KCl from
21 to 487 nm

Silver agglomerates
from 40 to 300 nm



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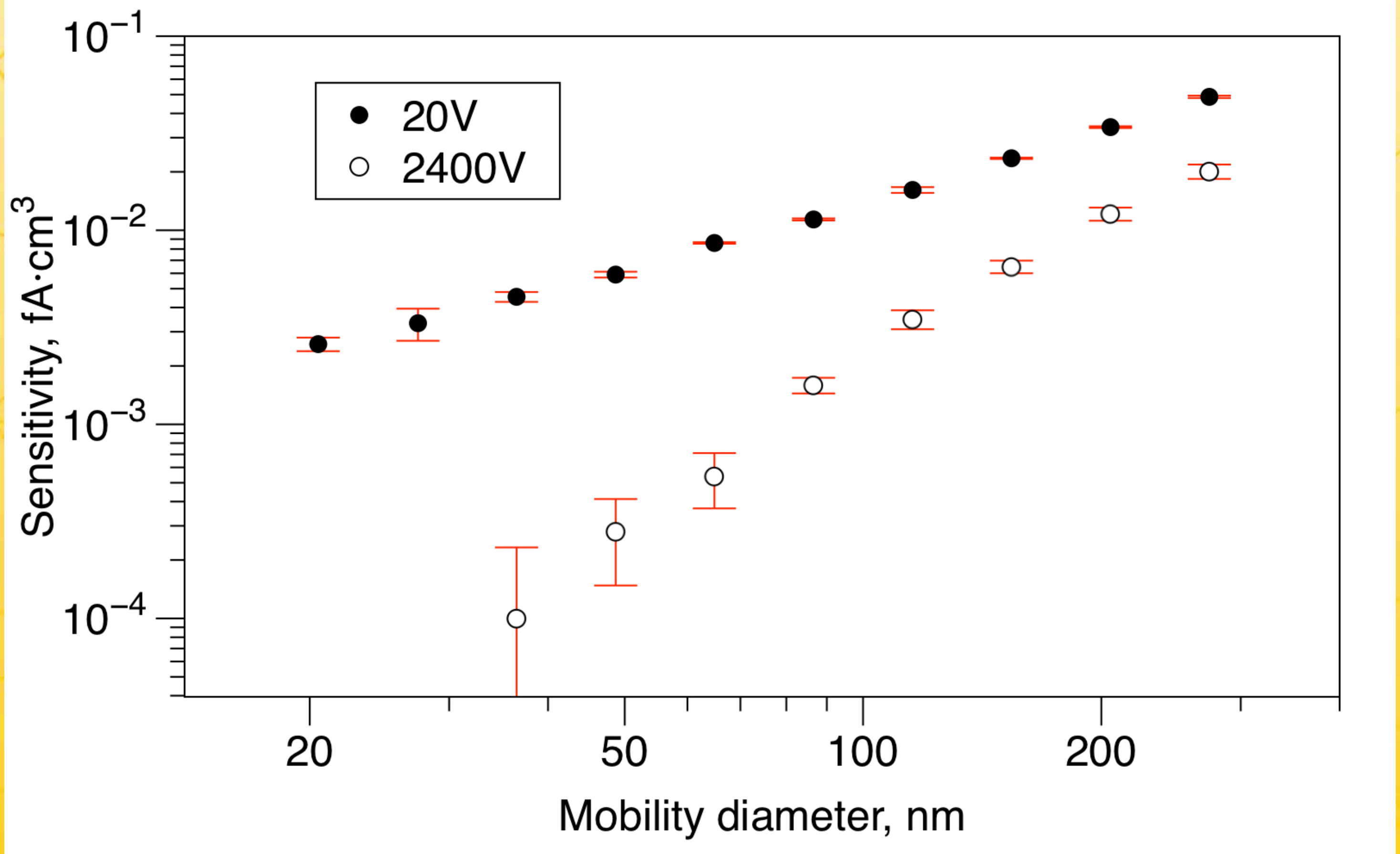
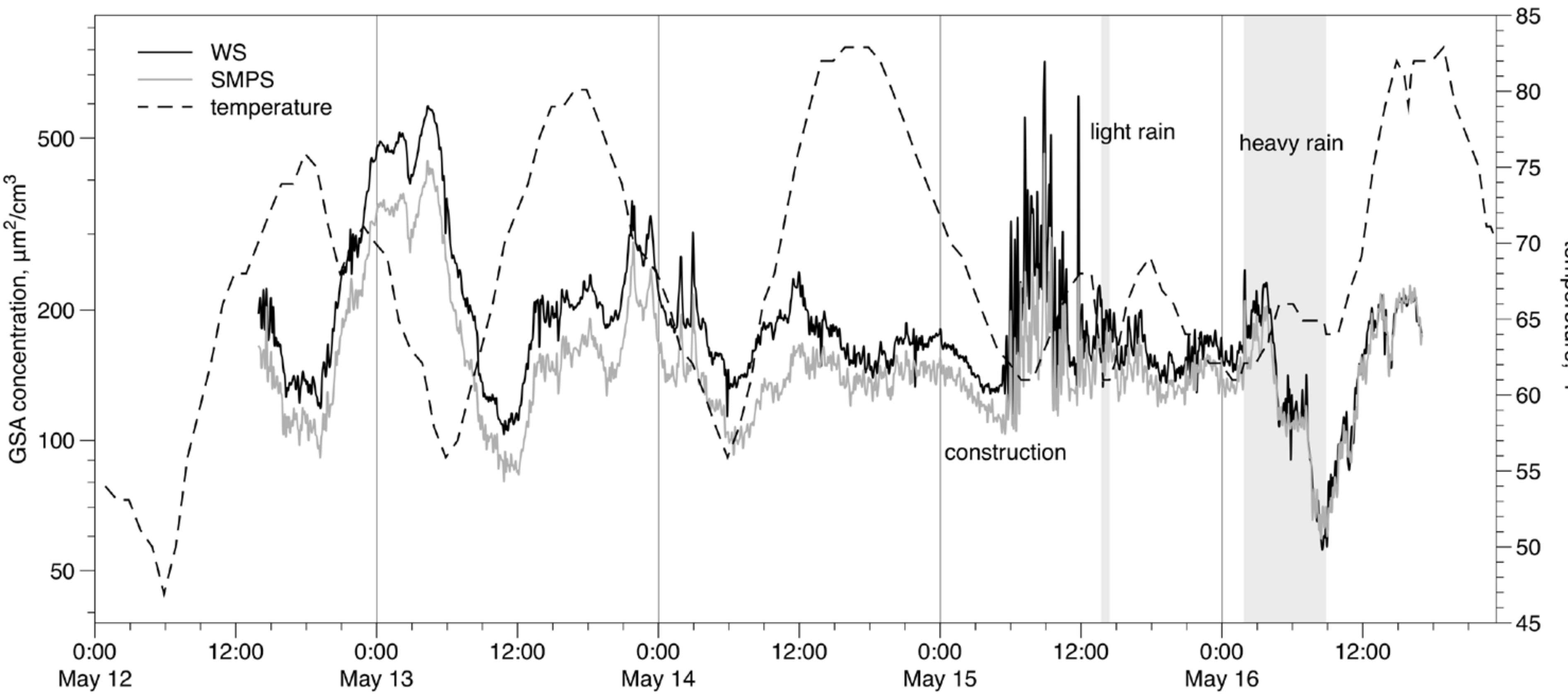
Appendix 2.2 Sensitivity at different voltages



Appendix 3. GSA concentration vs. temperature



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