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

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Outline

- ❑Background and objective
- ❑Methodology
- ❑Experiments
- ❑Summary

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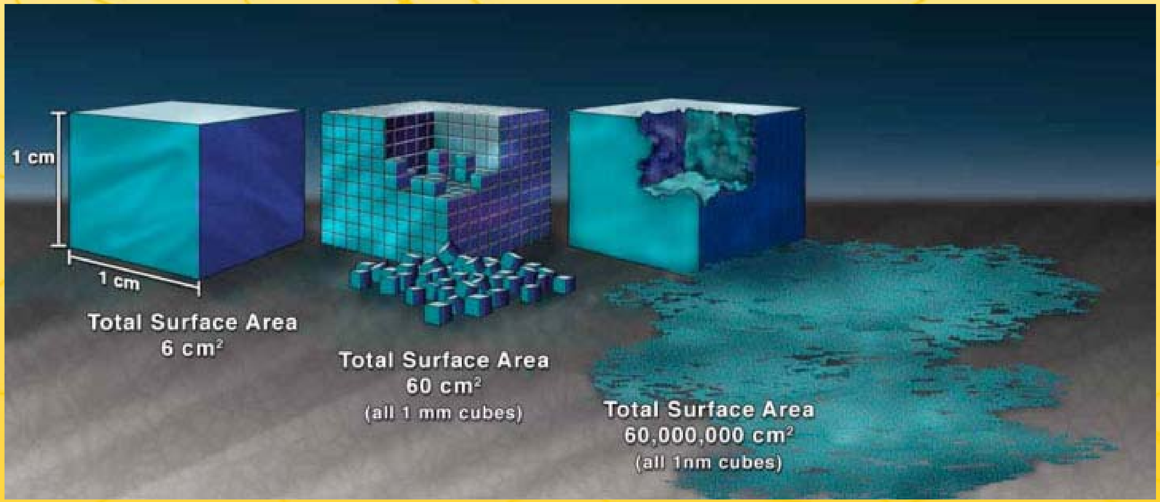
Significance of surface area



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

1 → 10,000,000x surface area

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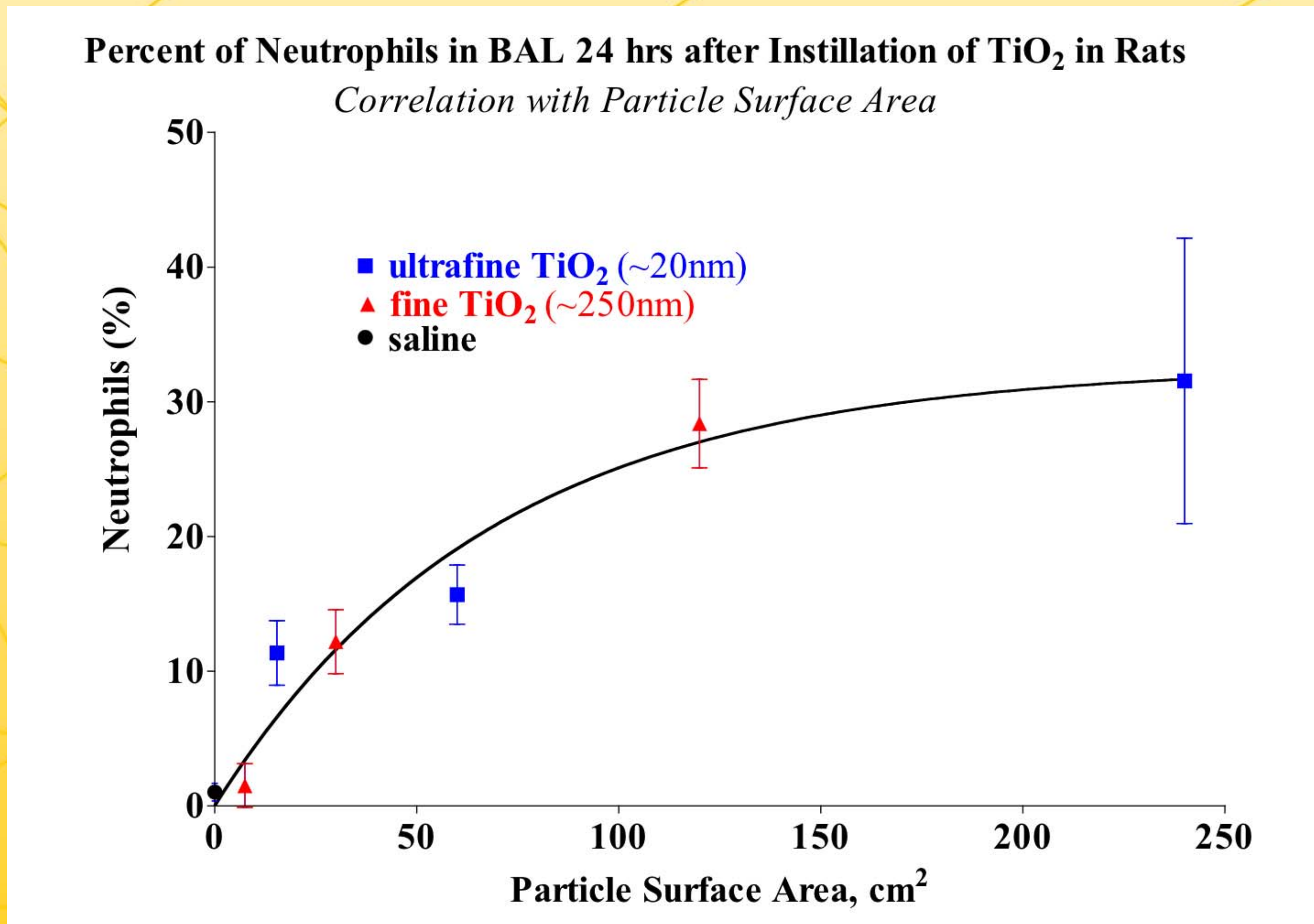
Health effect

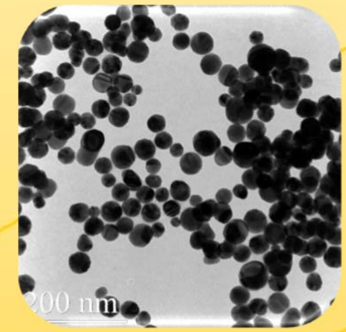


Oberdörster, G. (2000). Pulmonary effects of inhaled ultrafine particles. *International archives of occupational and environmental health, 74*(1), 1-8.

Methods for surface area: offline

BET method (gas adsorption):

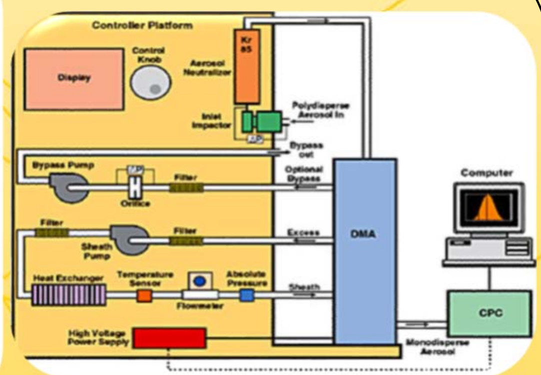
- Surface area including pores
- Direct (standard)
- Ex situ
- Time consuming
- Costly



Electron microscopy (TEM and SEM):

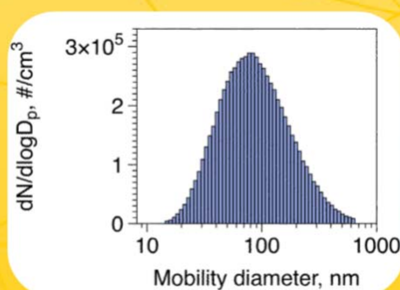
- 2D projected area
- Ex situ
- Time consuming
- Costly

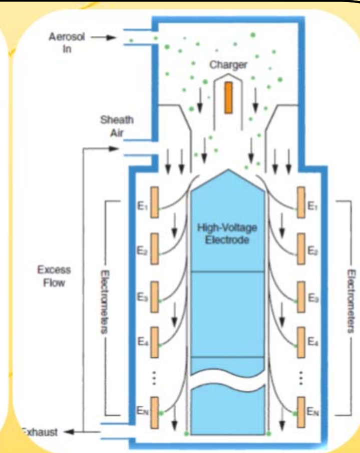
Methods for surface area: online



Scanning Mobility Particle Sizer (SMPS) Spectrometer:

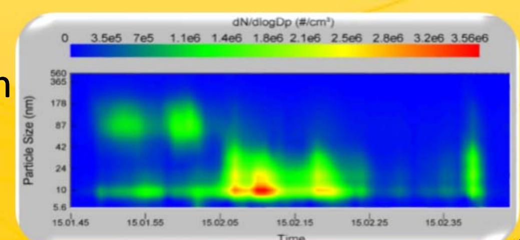
- Mobility diameter based distribution
- Minutes
- Bulky
- Working fluid
- Radiation source
- Costly





Fast Mobility Particle Sizer (FMPS) Spectrometer:

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



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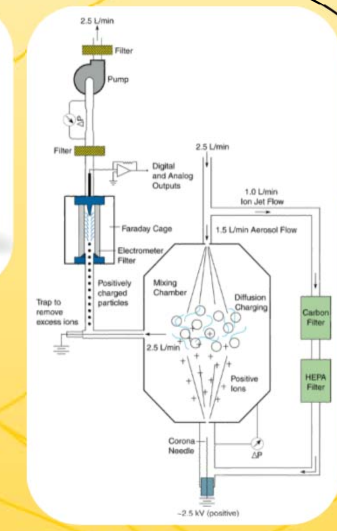
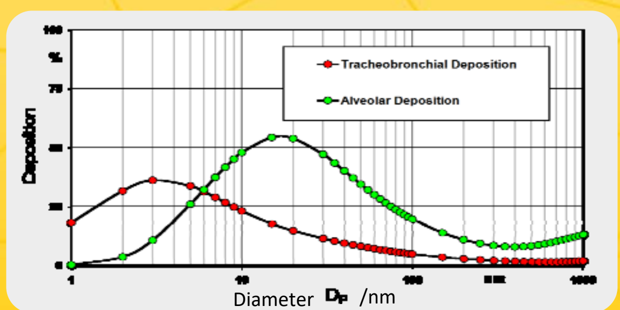
Methods for surface area: online 2



Nanoparticle Surface Area Monitor (NSAM):

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



So far, none quick and easy way to measure the geometric surface area (GSA) of particles

Objective

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

Features:

- Real time, GSA
- Transportation friendly: no working fluid, no radiation source, light-weight, and field portable.

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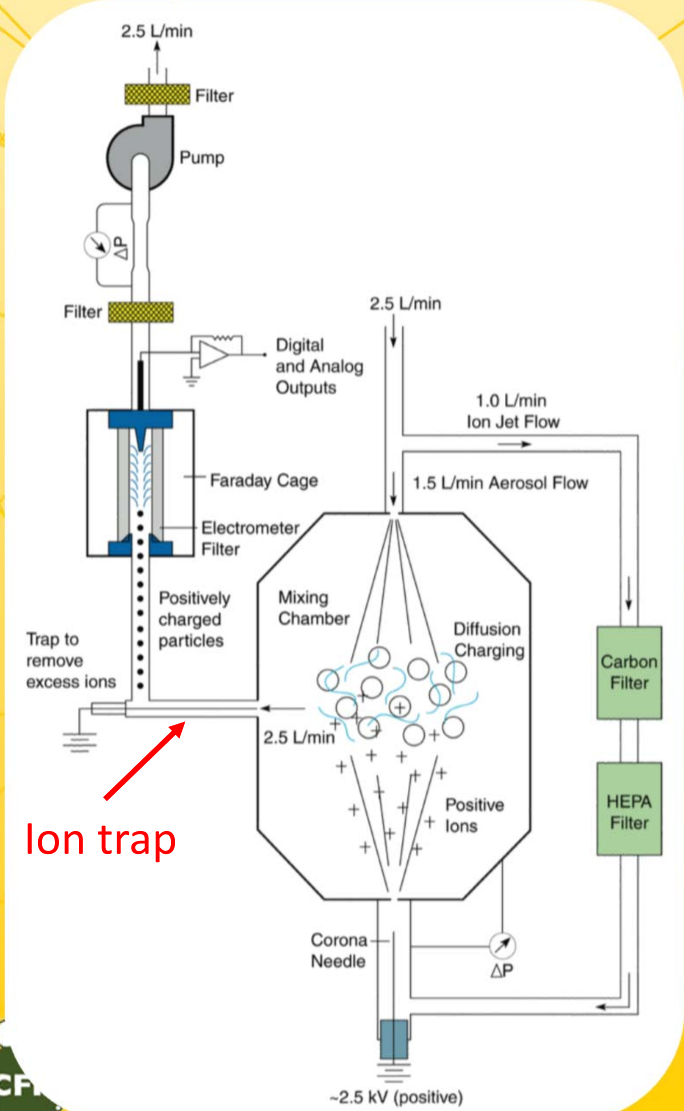
Methodology

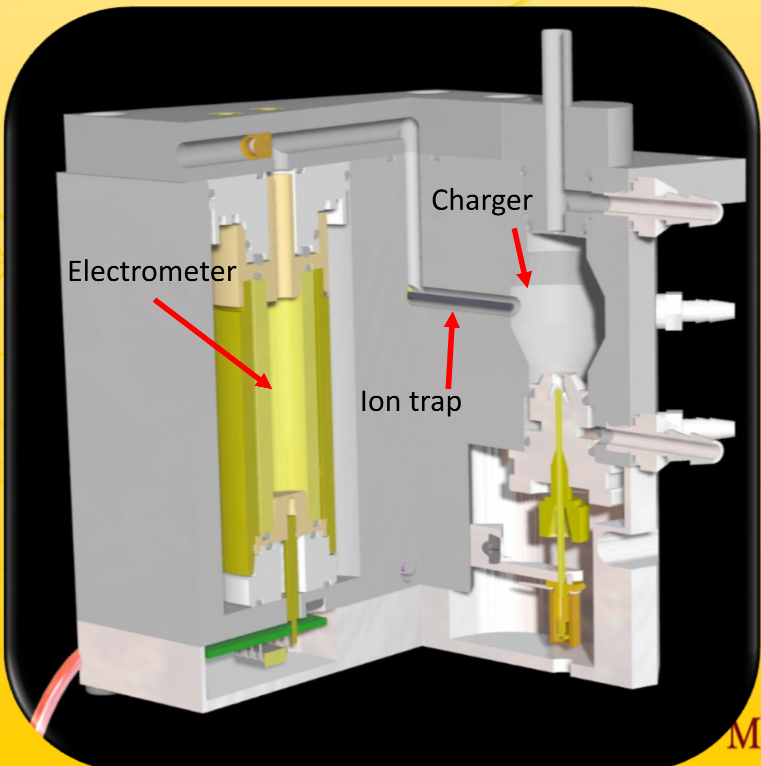
- Using Nanoparticle Surface Area Monitor (NSAM) as the basic tool

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

Appendix 1

NSAM
(Nanoparticle Surface Area Monitor)





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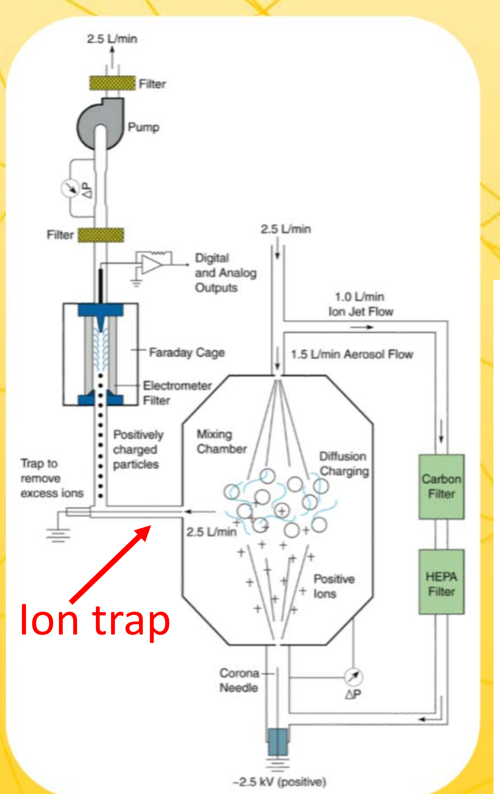
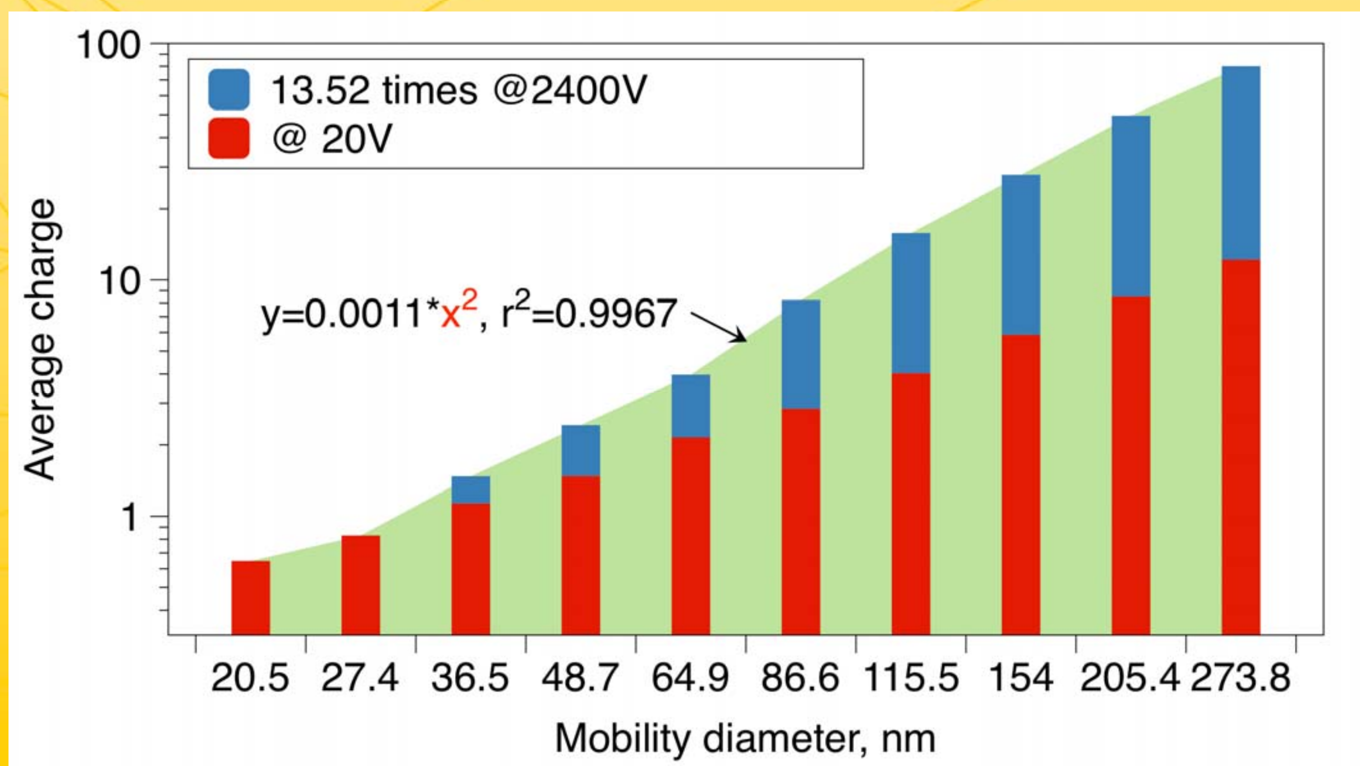
Changing voltage of ion trap

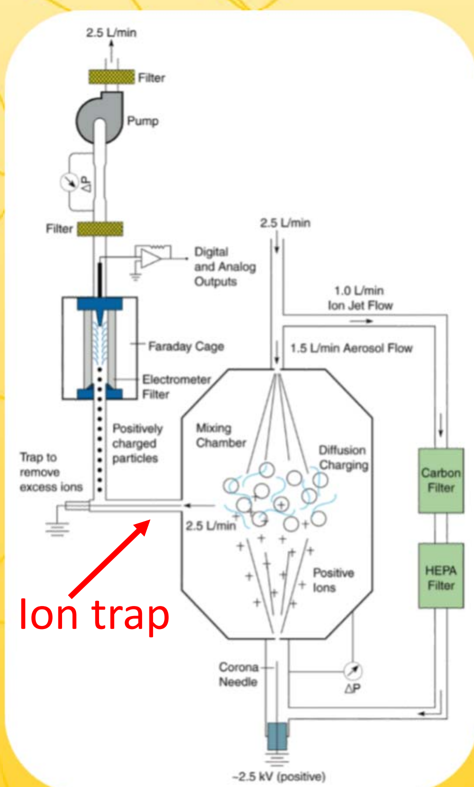
Combining electrical current under different voltages

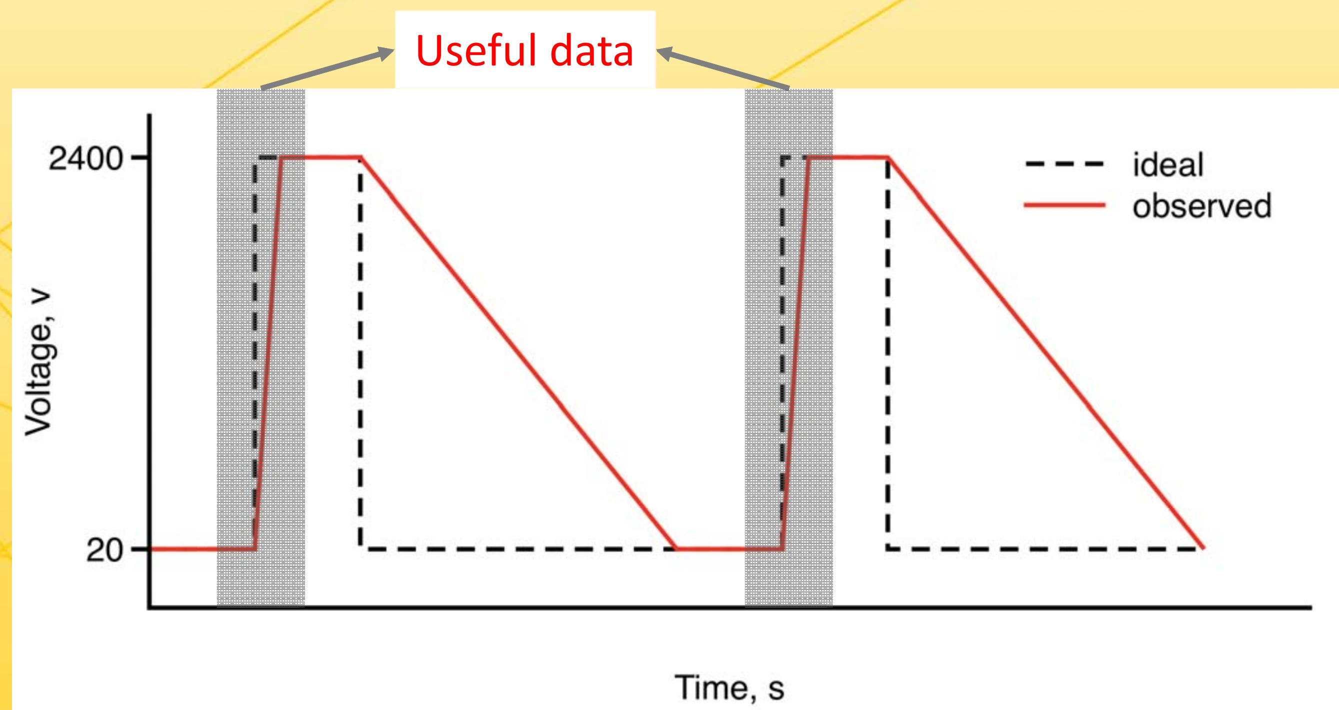
Average charge of particle ∝ surface area





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





LabVIEW-controlled voltage pulse makes the continuous sampling.

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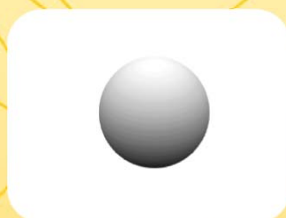
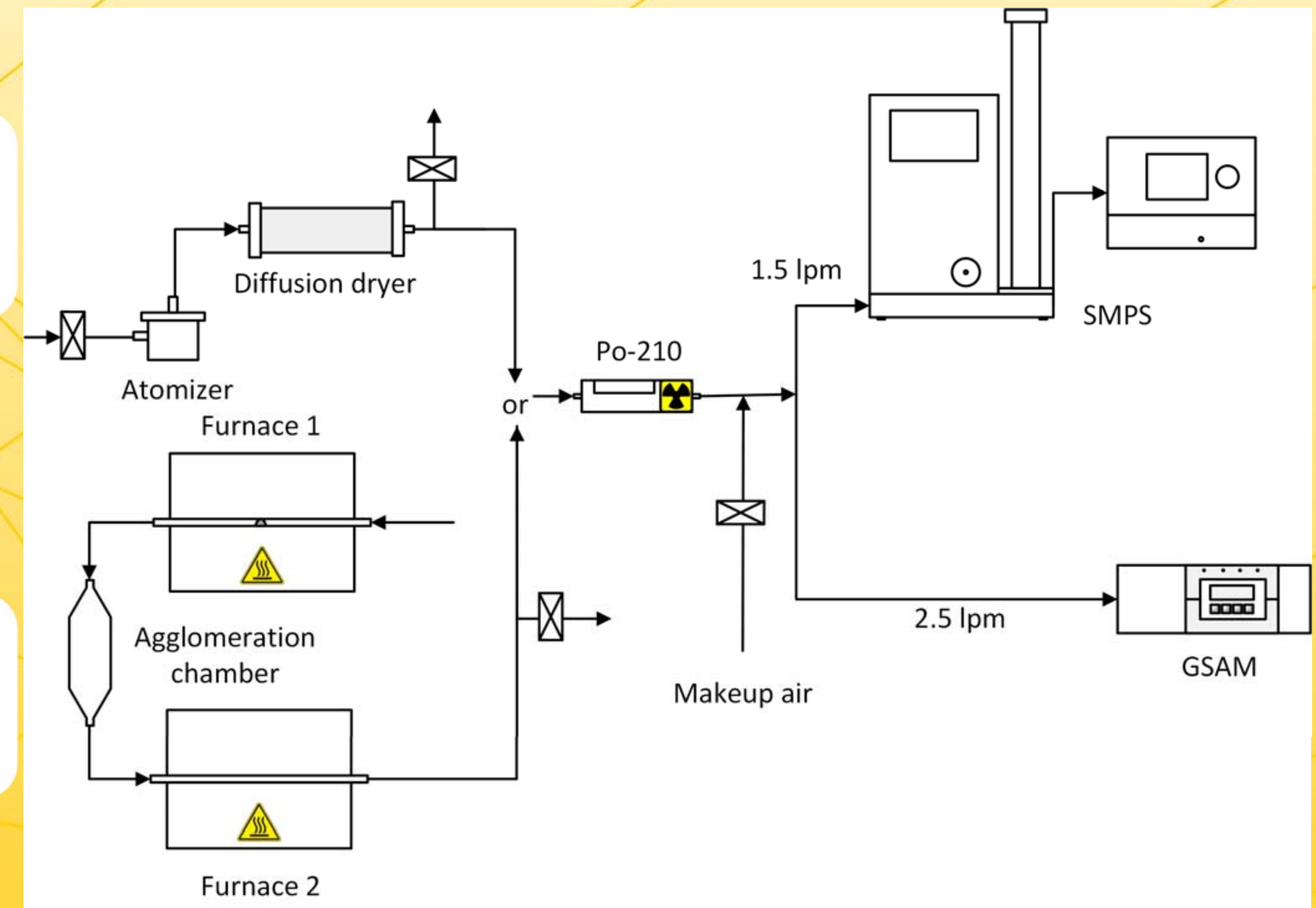
1. Validation in lab



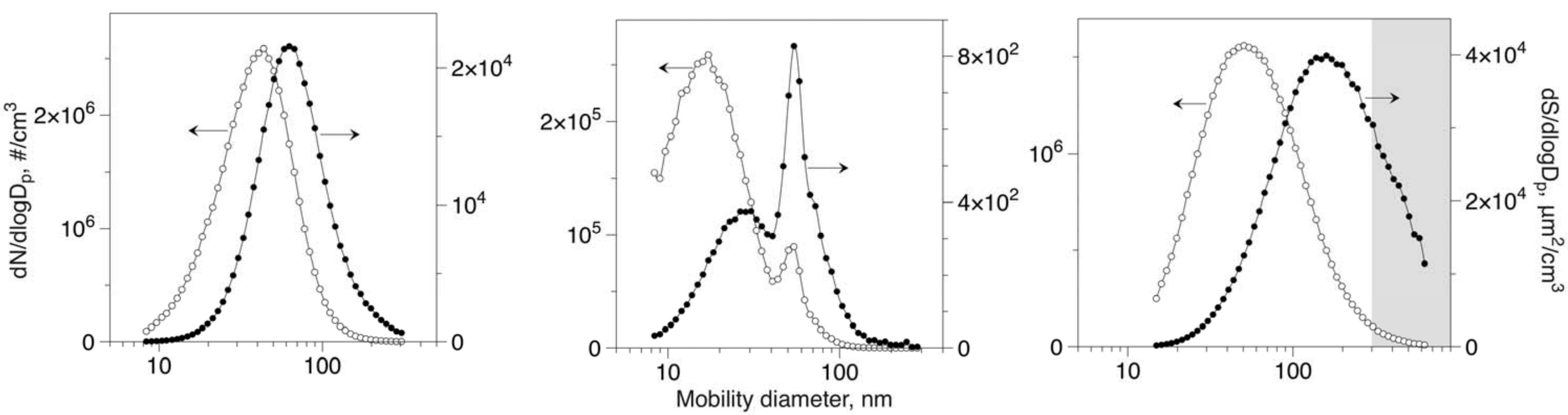


- The neutralized polydisperse aerosols were measured by GSAM and SMPS in parallel.
- Geometric surface area concentrations were compared to test the accuracy of the GSAM.

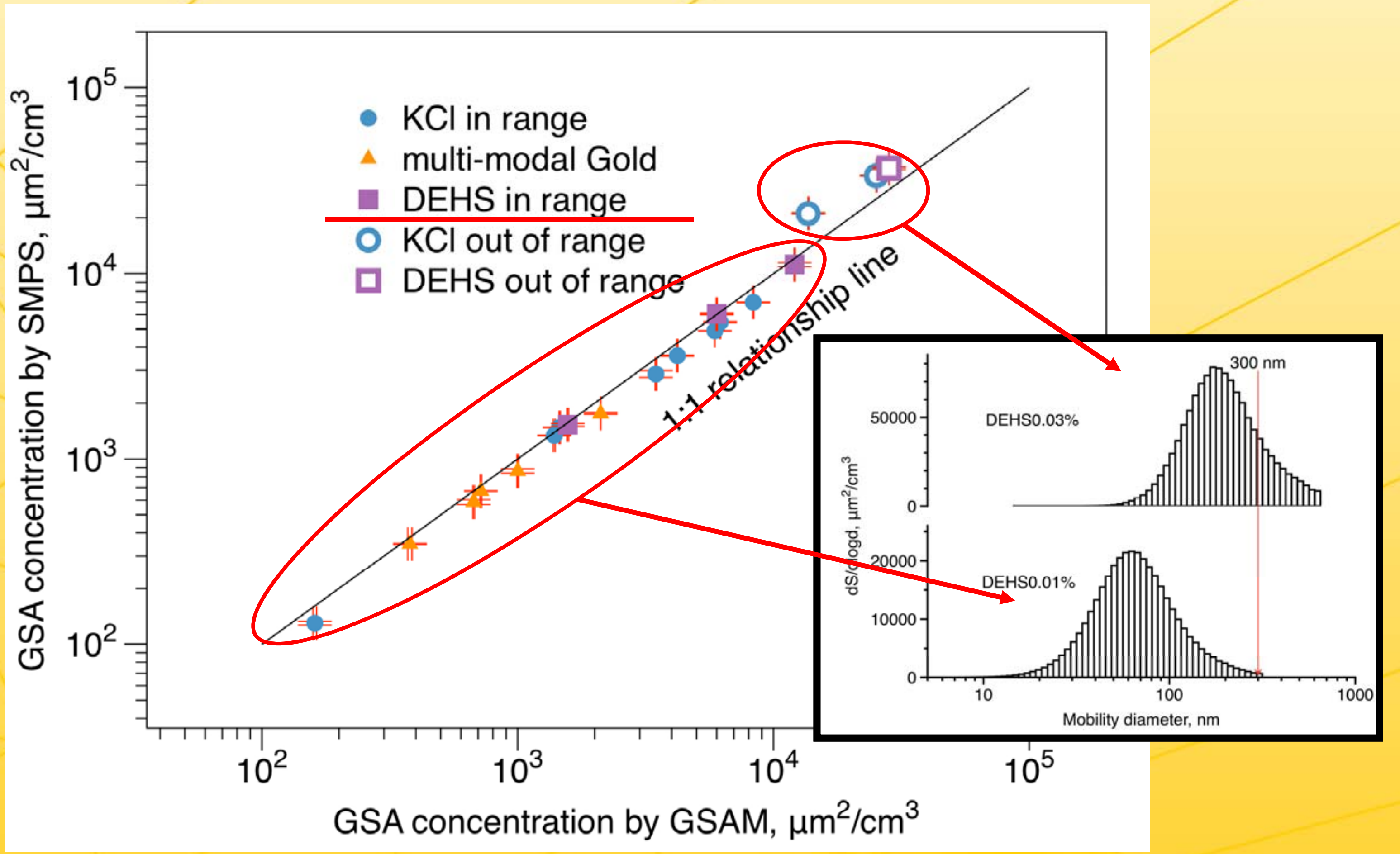
Appendix 2 for calibration

Test aerosol from atomizer

1. KCl, SiO_2, Au(gold), PSL(Polystyrene Latex), DEHS(Di-Ethyl-Hexyl-Sebacat).
2. Surface area distribution: 20-300 nm, range of accurate measurement
3. Surface area distribution: >300 nm, outside accurate range
4. Multi-modal distribution

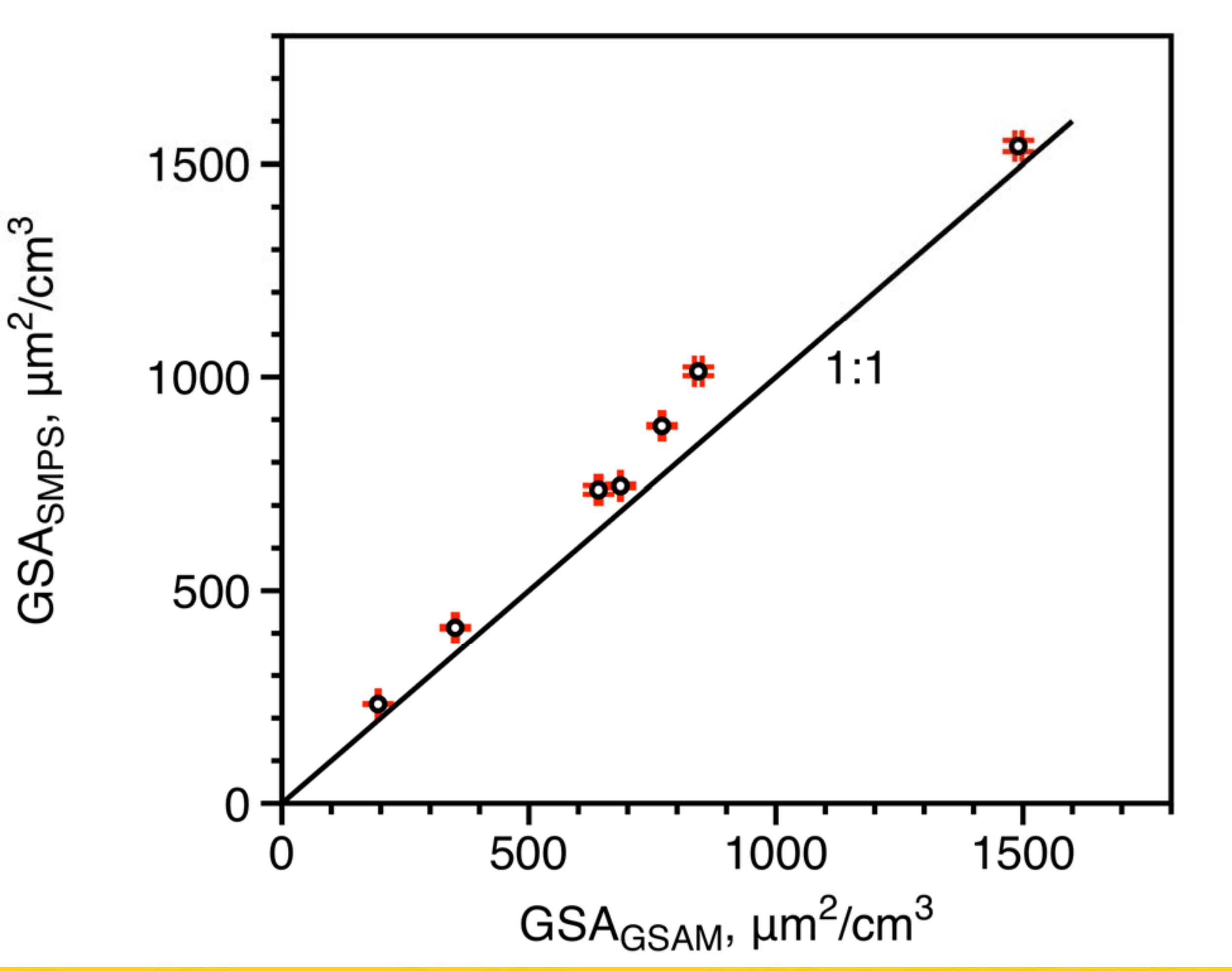


SMPS vs. GSAM (spheres)

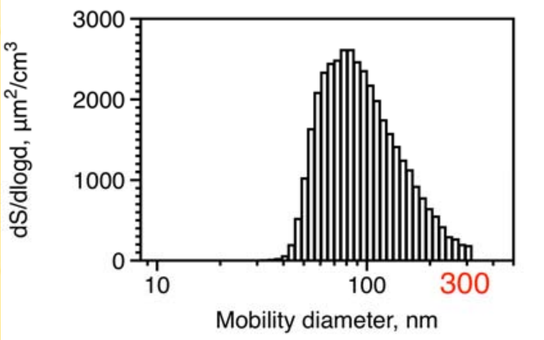


GSAM works great for 20-300 nm; works fine for >300 nm.

SMPS vs. GSAM (agglomerates)



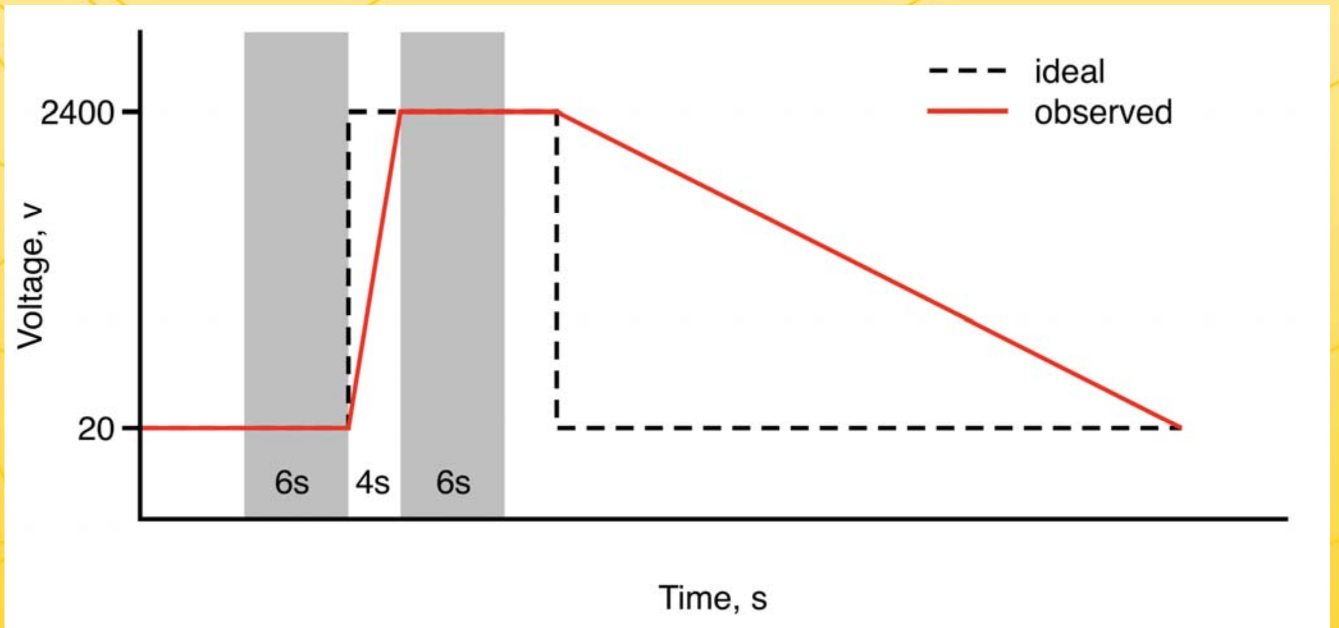
Data for SMPS are using agglomerate correction with primary particle size: 13.8, 16.2, 19.5 *nm* with *(*Wang et al., 2010; Kim et al., 2009; Shin et al., 2010.*)*



Calibration curve for spheres works fine for agglomerates.

2. Field measurement

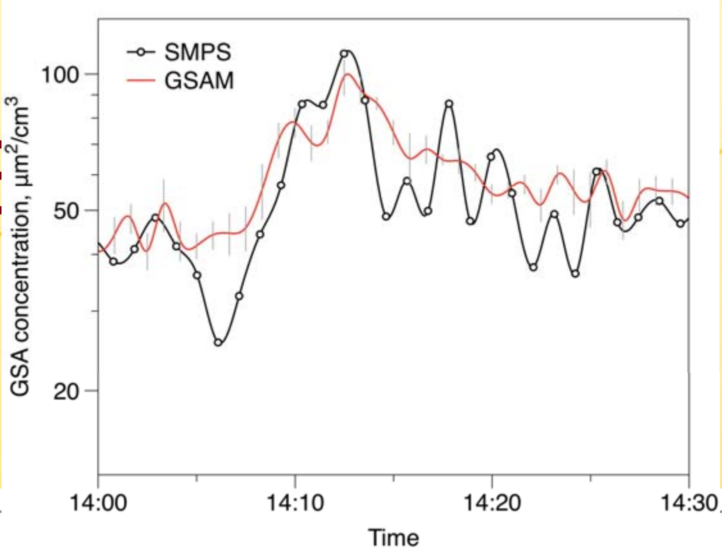
- Parallel sampling using GSAM and SMPS
  - SMPS: one sample every 62 s (17.5-532.8 nm)
  - GSAM: one average value for every 50 s. 12 s for sampling and 38 s for stabilizing voltage

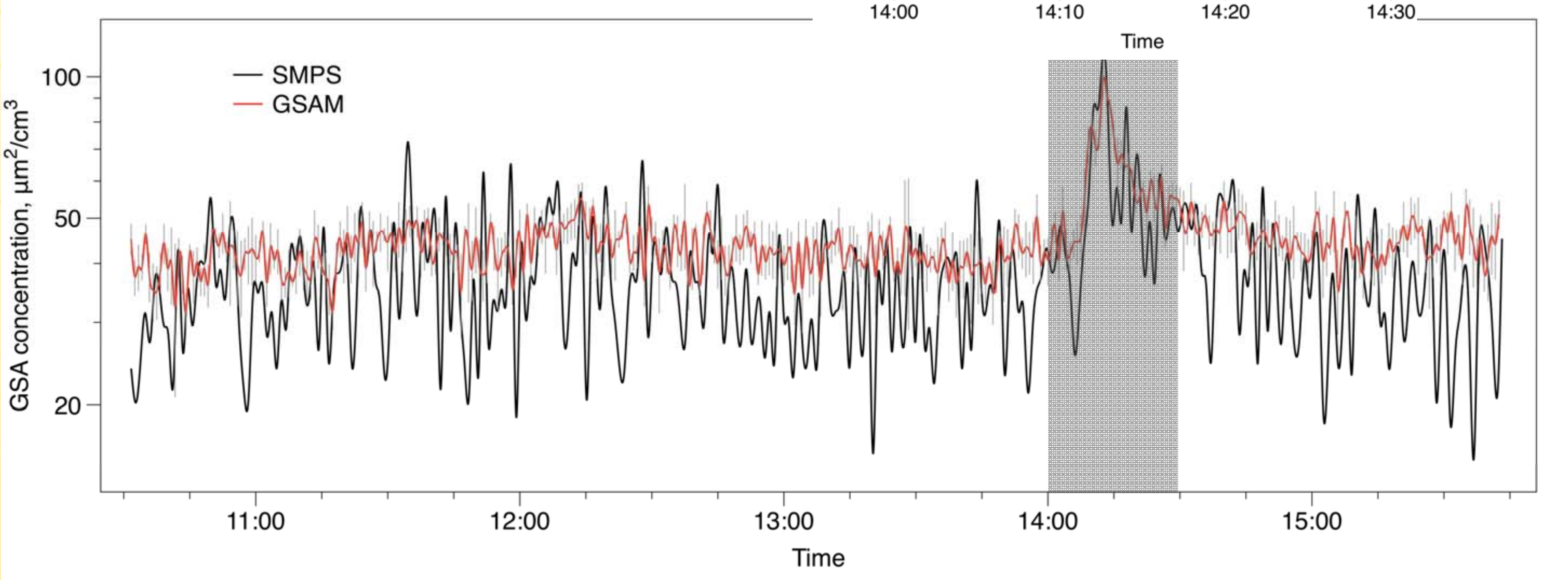


- Location or event: lab 4130, outdoor, laser printing, grinding, waterjet cutting, welding

Lab ME

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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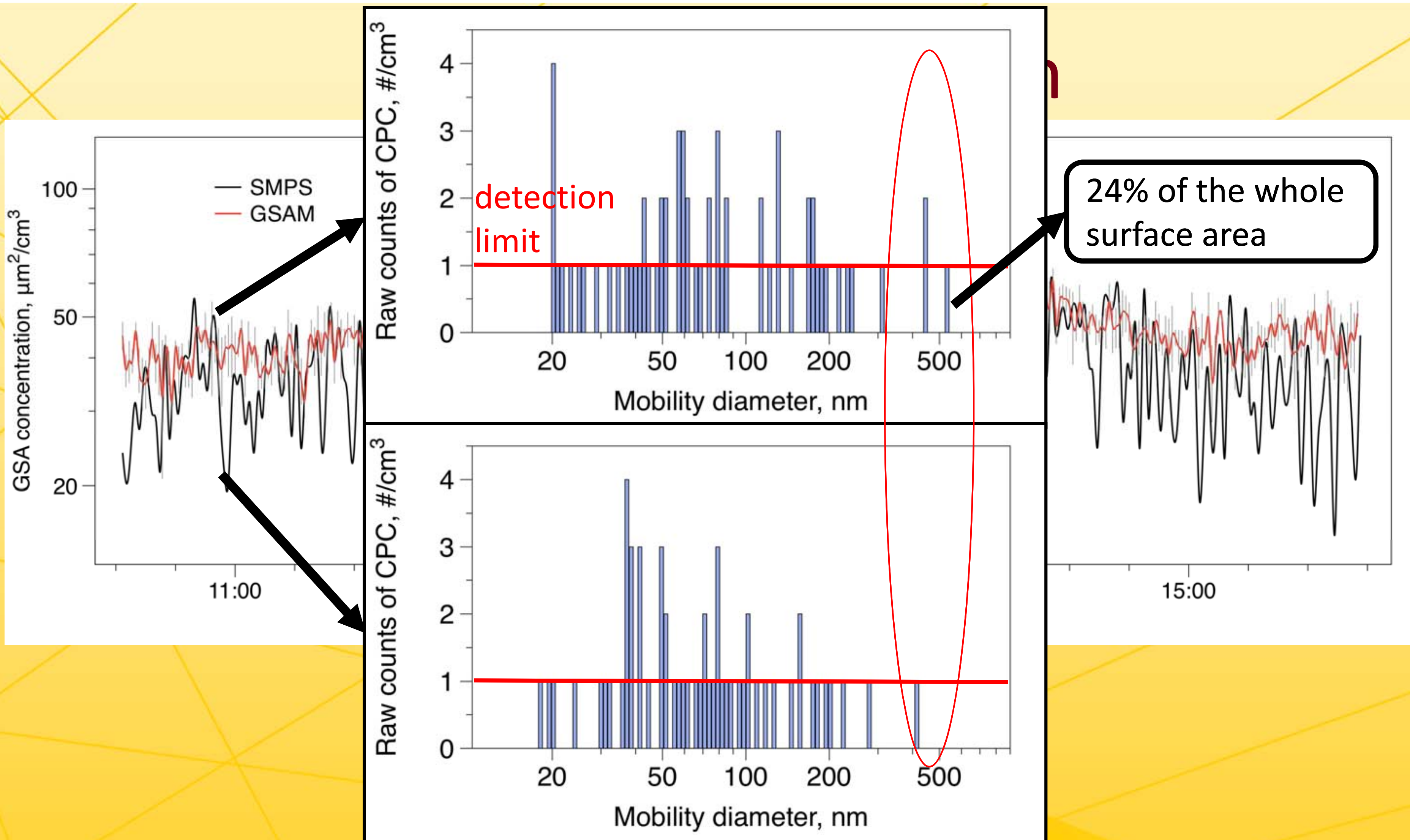

	GSAM	SMPS (CPC)
Detection limit (DL)	1 fA	1 #/cm^3
Lowest signal here	4.8 fA (4.8 times of DL) ✓	1#/cm^3 (1 time of DL)

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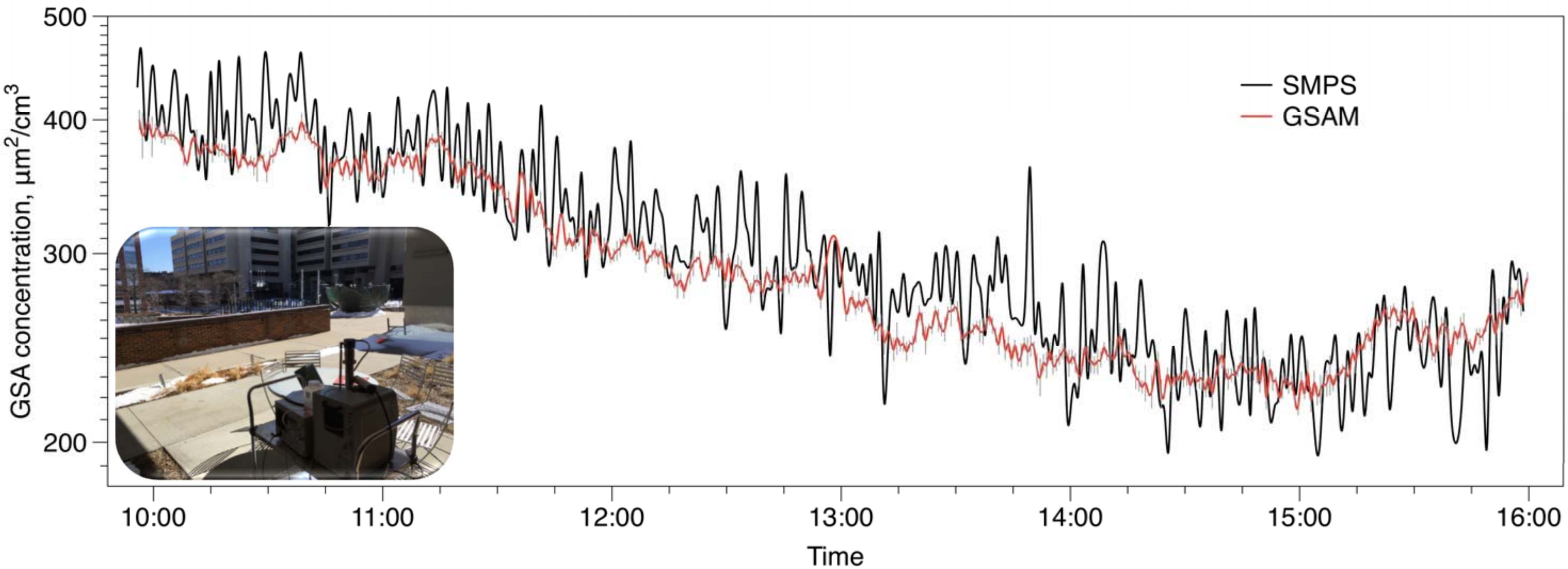
Outdoor

Sampling length: ~6 hours



The trend and concentration were both well captured by GSAM for outdoor aerosol.

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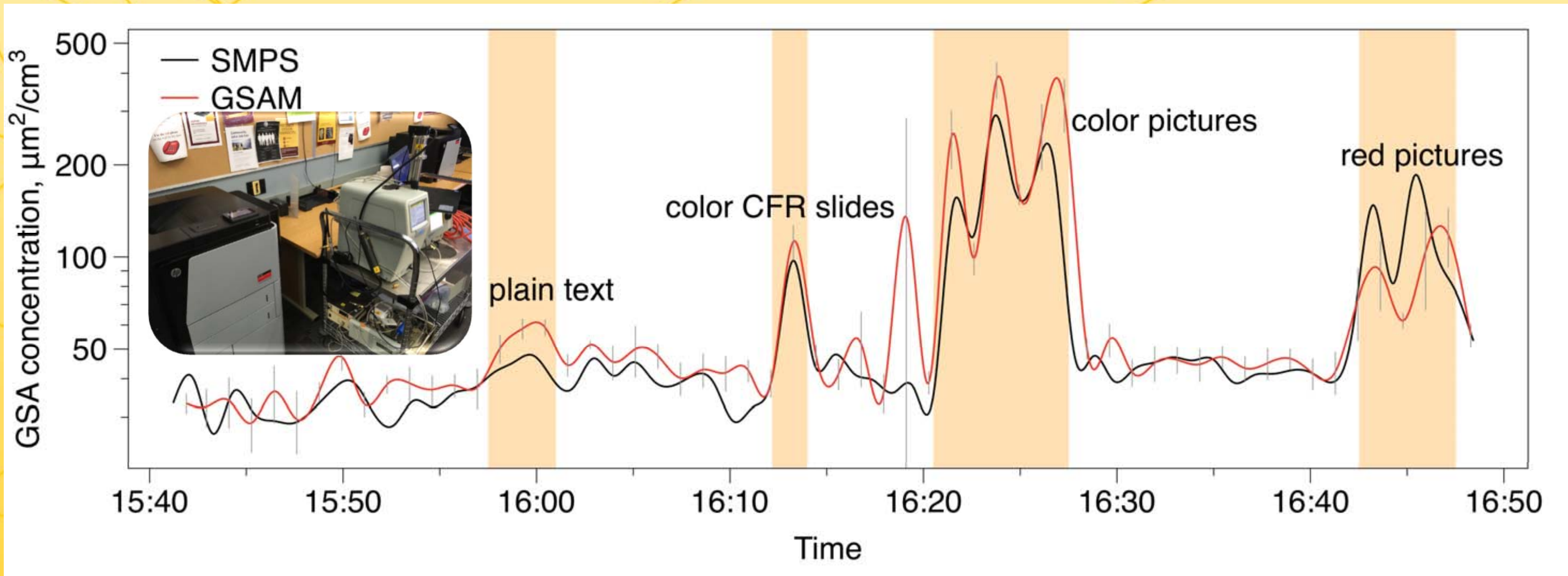
Laser printer in computer lab

Sampling length: ~1 hour



- For wide variation of GSA concentrations, GSAM is accurate.
- Large error bars are due to transient emission.

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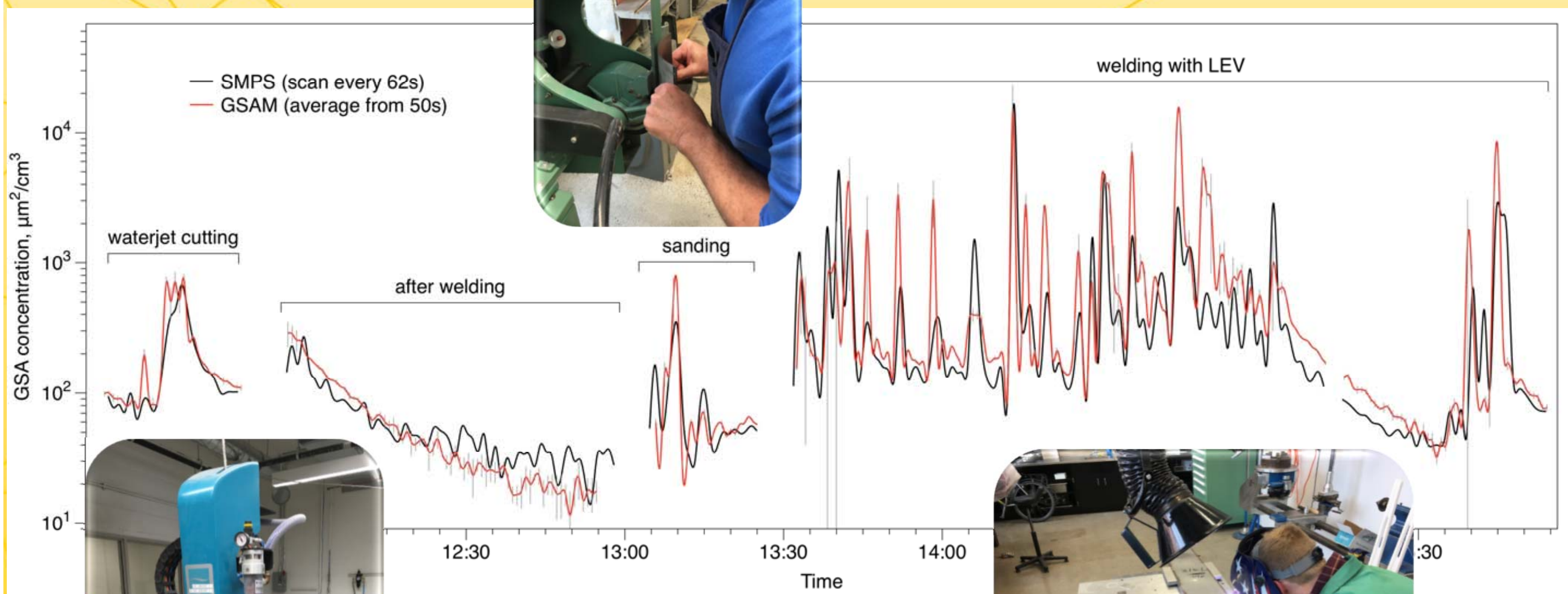
Machine shop

Sampling length: ~4.5 hours



- The trends agree with each other.
- Transient emission are difficult for both instruments.

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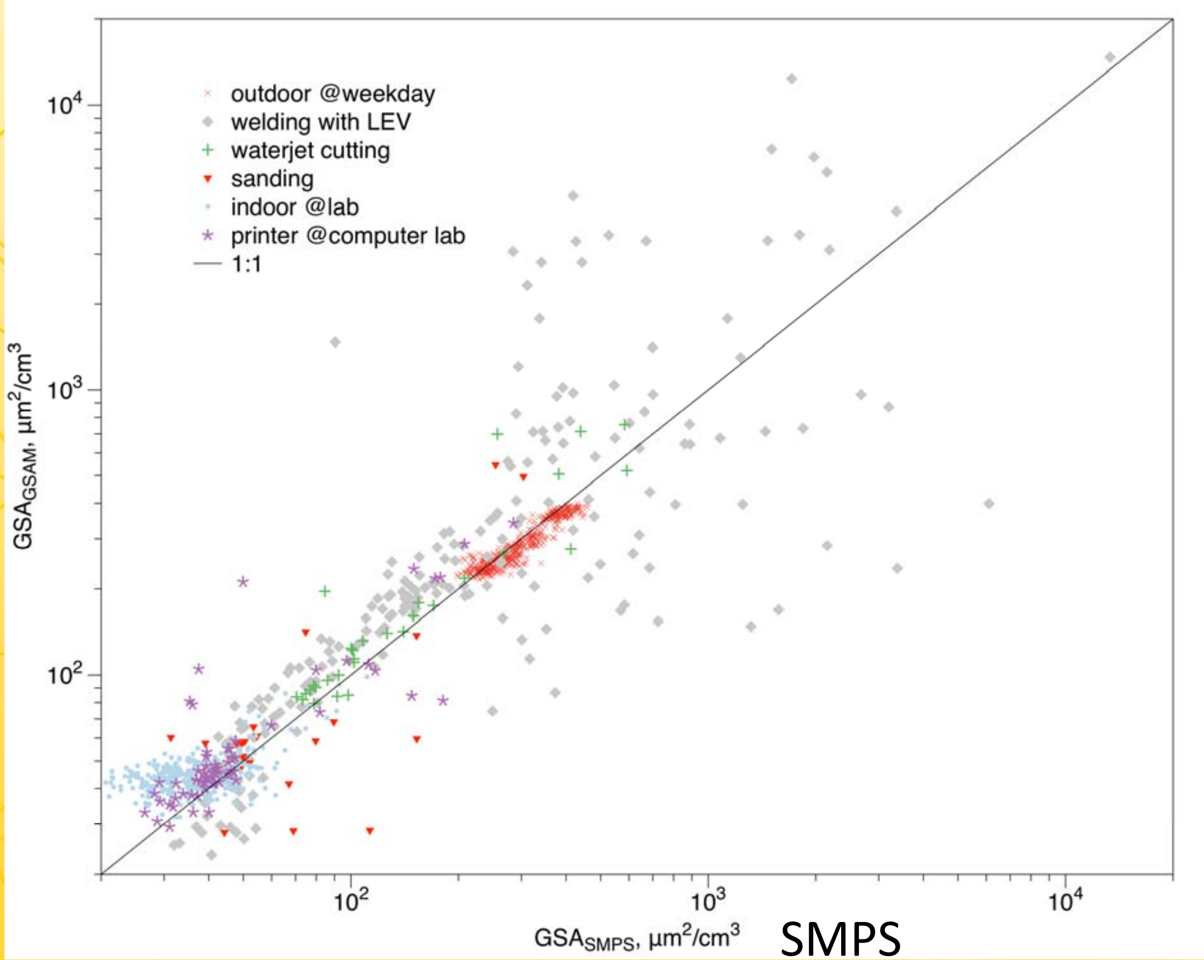
Correlation between GSAM and SMPS

GSAM



SMPS

- Overall, both measurements agree well with each other.
- Discrepancy comes from the particle shape and transient emission.

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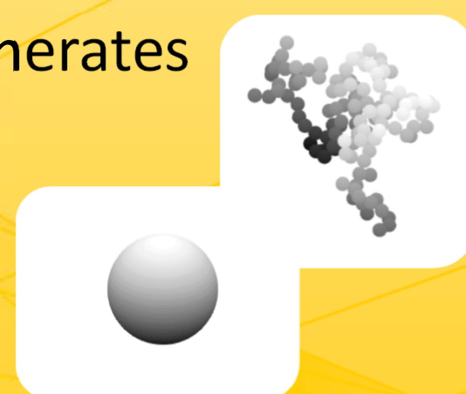
Summary

The novel GSAM successfully measures the GSA of both lab-generated and real environment particles with the following features:

- In a wide range: 20 to 530 nm
- Possibly time resolution can be within several seconds
- For the mixture of spheres and agglomerates
- For both indoor and outdoor
- Cost-effective and field-portable
- With simple setup



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Thank you

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Major reference

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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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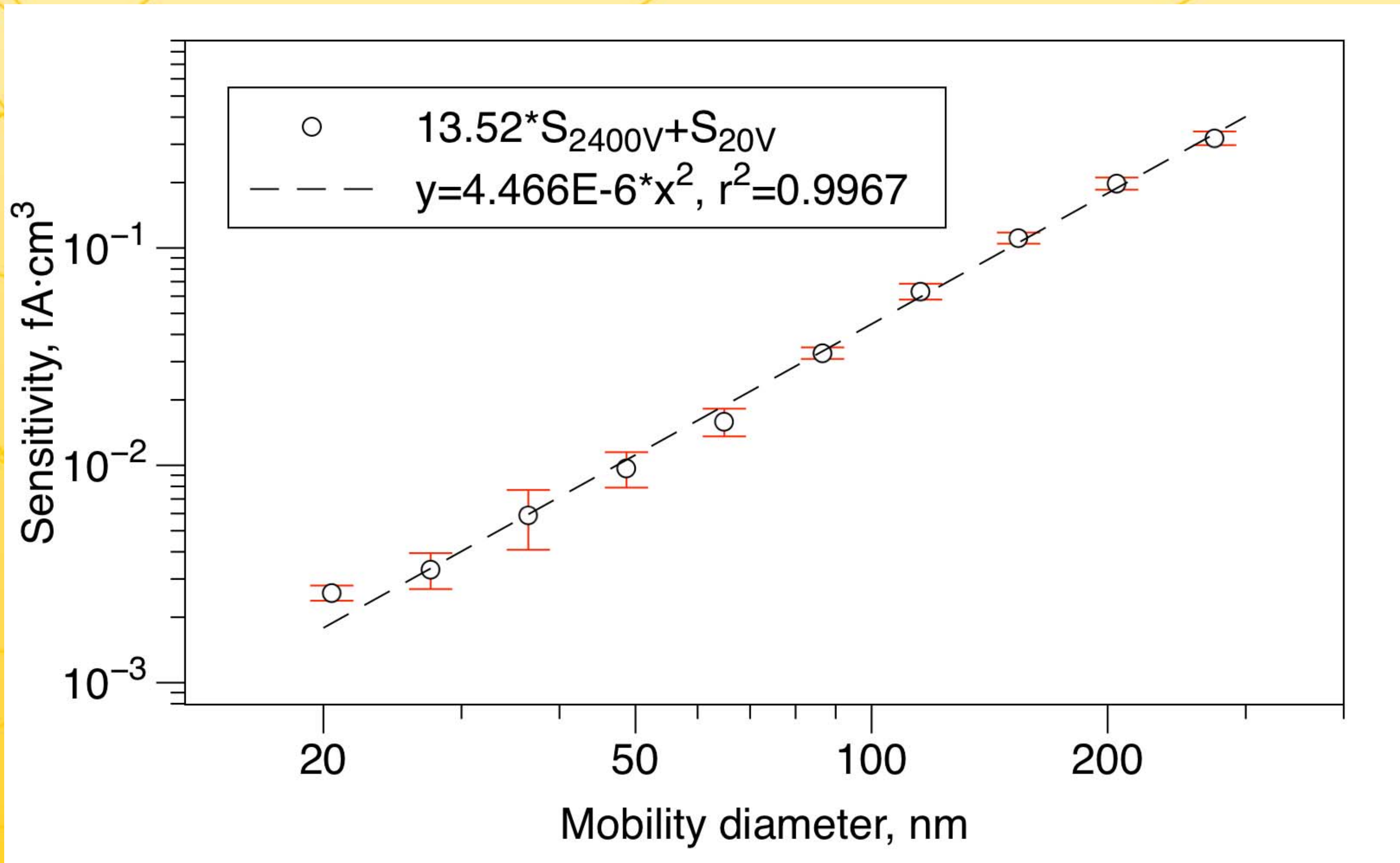
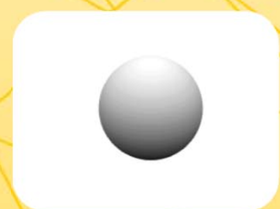
Appendix 1.2 Sensitivity fitting



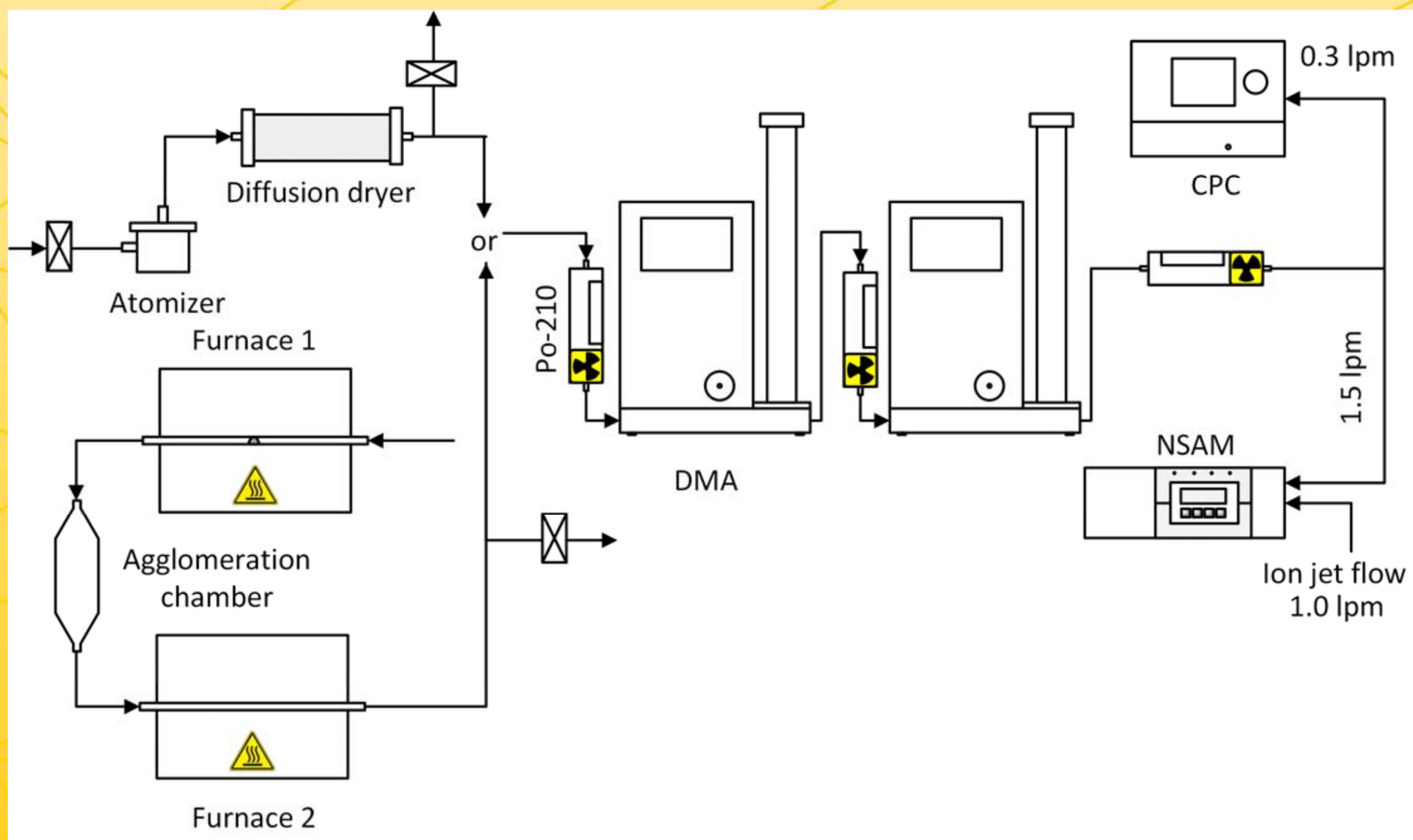
Appendix 2.1 Sensitivity of the monitor:

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



KCl from
21 to 487 nm

Silver agglomerates
from 40 to 300 nm



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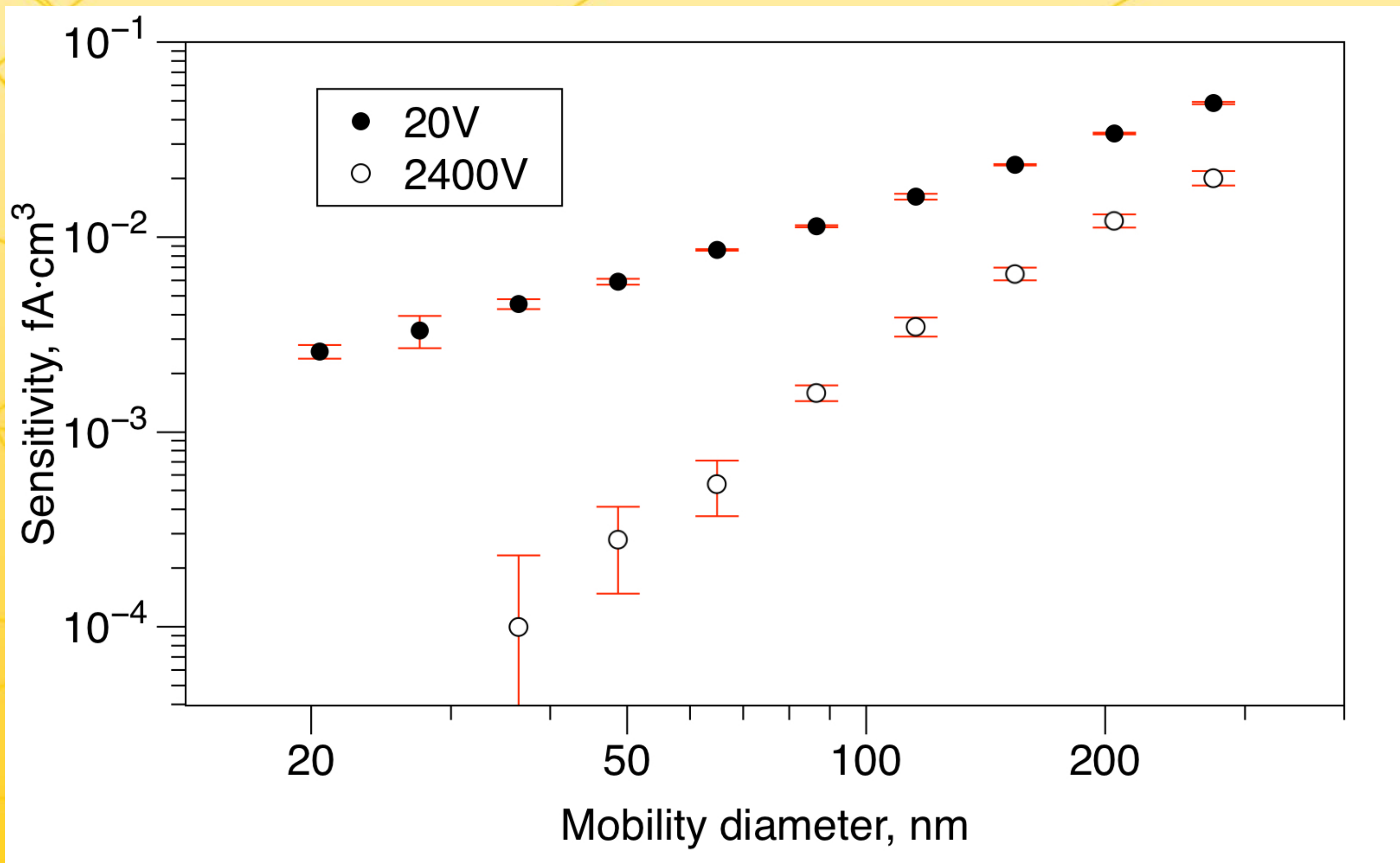
Appendix 2.2 Sensitivity at different voltages



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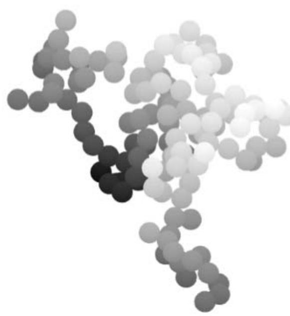
Appendix 3. GSA for agglomerates

$$Instead\ of\ S(d) \propto d^2, we\ need\ S(d) \propto GSA\ for\ agglomerates$$

GSA of one agglomerate by Sorensen, 2001:

$$\pi N_{pp} d_{pp}^2 = \pi d_{pp}^{-0.17} d_m^{2.17}, N_{pp} < 100,$$
$$\pi N_{pp} d_{pp}^2 = 2.16\pi d_{pp}^{0.21} d_m^{1.79}, N_{pp} > 100$$



GSA of one agglomerate by Lall & Friedlander, 2006:

$$\pi N_{pp} d_{pp}^2 = \frac{12\pi^2 \lambda d_m}{c^* C_c(d_m)}$$

Where N_{pp} is the number of primary particle, d_{pp} is the diameter of the primary partilce, d_m is the mobility diameter, C_c is the slip correction, c^* is the dimensionless drag force and λ is the mean free path of the gas.