Specific BET Surface Area Measurement of Low-Mass-Samples

E. Karg, G. A. Ferron, G. Schumann and O. Schmid
Institute for Inhalation Biology, Helmholtz Center Munich, D-85758 Neuherberg/Munich, Germany

Keywords: Aerosol sampling, black carbon, particle characterization, measurement errors, BET specific surface area of particles.

Introduction

The specific surface area (SSA) of carbonaceous particles has shown better correlation with biological effects than other parameters such as particle diameter or organic content (Oberdörster et al., 2005; Stoeger et al., 2006; Stoeger et al., 2007). However, especially for particles with low SSA, relatively large amounts of sample (here: up to 100 mg) are needed for reliable BET surface area measurements. In this study we present an analysis of systematic errors in SSA due to low sample mass and describe how to define the lower detection limit of the instrument and how to correct for these errors.

Method

Up to seven samples with different mass from four types of carbonaceous particles were analyzed with an automated BET sorptometer (Porous materials Inc., USA) with nitrogen as test gas molecules. All data were taken at isothermal conditions at the boiling point of nitrogen (77 K). Sample preparation included surface cleaning by thermal desorption during a 2 hr period at 20 µTorr (vacuum) and 250 °C.

The measured SSA (SSA_m) data were fitted according to

$$SSA_m = \frac{A_d + A_p}{M_p} = \frac{A_d}{M_p} + SSA_o \qquad (1)$$

where A_d is assumed to be a virtual internal surface area of the instrument, A_p is the particle surface area of the sample, M_p is the sample mass and SSA_o is the true SSA of the particles.

Results and Discussion

For each material, the parameters A_d and SSA_o were determined by fitting equation (1) to the data sets (Figure 1).

All fits showed regression coefficients better than 0.89 and $p < 0.02$. The fit parameters SSA_o agree with SSA_s (given by the suppliers) within 22 % (see Table 1).

For a better estimate of A_d, all SSA_m values were normalized with the material's SSA_o and plotted against the particles' surface area $A_p = M_p\ SSA_o$ (Figure 2). This transformation allows to incorporate all data into one single fit yielding a more reliable A_d of 0.33 m². As indicated there, the data provide correct SSA values (bias = 1) only for sufficiently large surface areas (or sample mass).

For the BET instrument used here, a standard deviation of 7.5 % was found for samples of sufficient high mass. Therefore, two different regimes of bias can be distinguished: a bias > 7.5 % in SSA for samples with A_p smaller than about 5 m² and < 7.5 % for $A_p > 5$ m².

We hypothesize that A_d is evoked by blank and dead space corrections which are inadequate in accuracy for the low-mass problem.

Conclusions

The method presented here can be used to determine the lower threshold area $A_{p,t}$ (and the corresponding mass) to achieve results within the instrument's standard deviation. It additionally can be used to correct for biases in the measured SSA_m values assuming a virtual internal instrument surface area. Biases however are particularly pronounced for low-mass samples.

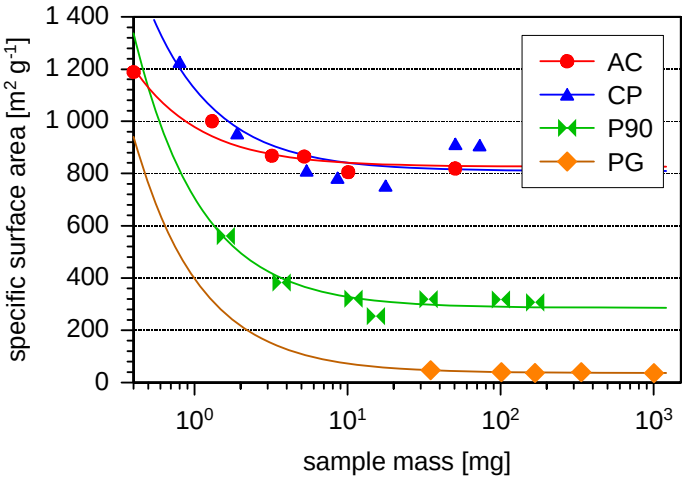


Figure 1. Specific surface area SSA_m vs. sample mass

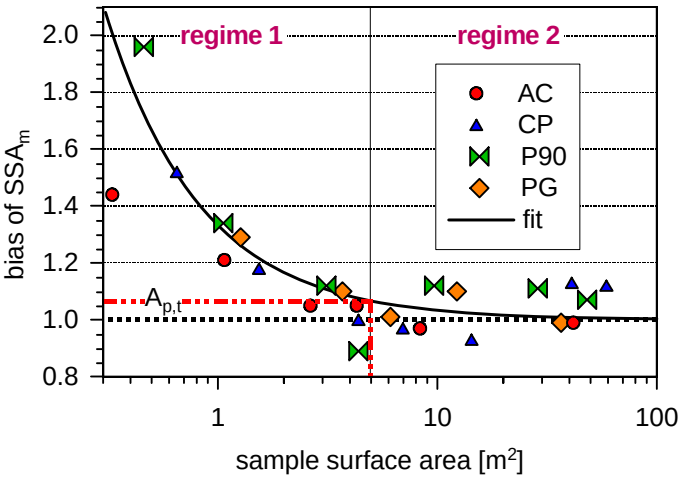


Figure 2. Normalized SSA vs. sample surface area A_p

Table 1. Materials and fit parameters. SSA_s: SSA provided by the supplier; R: regression coefficient (Figure 1); p: p-value of significance; $M_{p,min}$: minimum mass for a SSA bias < 10 %

	AC[1]	CP[2]	P90[3]	PG[4]
SSA_s [m²/g]	1000	n. a.	300	30
SSA_o [m²/g]	826	809	286	36.5
A_d [m²]	0.152	0.316	0.421	0.362
R	0.98	0.89	0.95	0.93
p	0.002	0.008	0.002	0.018
$M_{p,t}$ [mg]	4.0	4.1	11.5	90

[1] Activated charcoal, Merck # 1.09631; [2] Carbon Particles generated by electric spark discharge (PALAS, model GFG1000, Germany); [3] Pigment black, "Printex 90", Degussa, Germany; [4] Pigment black, "Printex-G", Degussa, Germany

Acknowledgements

We wish to thank Dipl. Ing. X. Hecht, Department of Chemistry, Technical University of Munich for providing the instrumentation and performing the measurements.

References

Oberdörster, G., Oberdörster, E., and Oberdörster, J. (2005). Nanotoxicology: An emerging discipline evolving from studies of ultrafine particles. Environmental Health Perspectives 113, 823-839.

Stoeger, T., Reinhard, C., Takenaka, S., Schroeppel, A., Karg, E., Ritter, B., Heyder, J., and Schulz, H. (2006). Instillation of six different ultrafine carbon particles indicates a surface area threshold dose for acute lung inflammation in mice. Environ Health Perspect 114, 328-333.

Stoeger, T., Schmid, O., Takenaka, S., and Schulz, H. (2007). Inflammatory response to tio2 and carbonaceous particles scales best with bet surface area. Environ Health Perspect *115*, A290-291; author reply A291-292.

HelmholtzZentrum münchen
German Research Center for Environmental Health

IHB
Institute for
Inhalation Biology

Specific BET Surface Area Measurement of Low-Mass-Samples

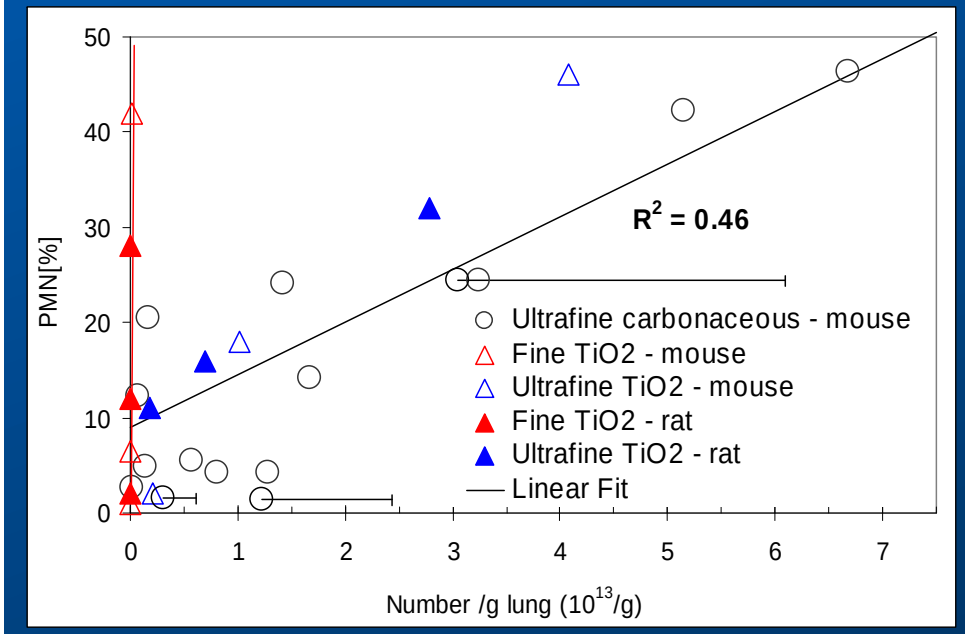
Erwin Karg, G.A. Ferron

and Otmar Schmid

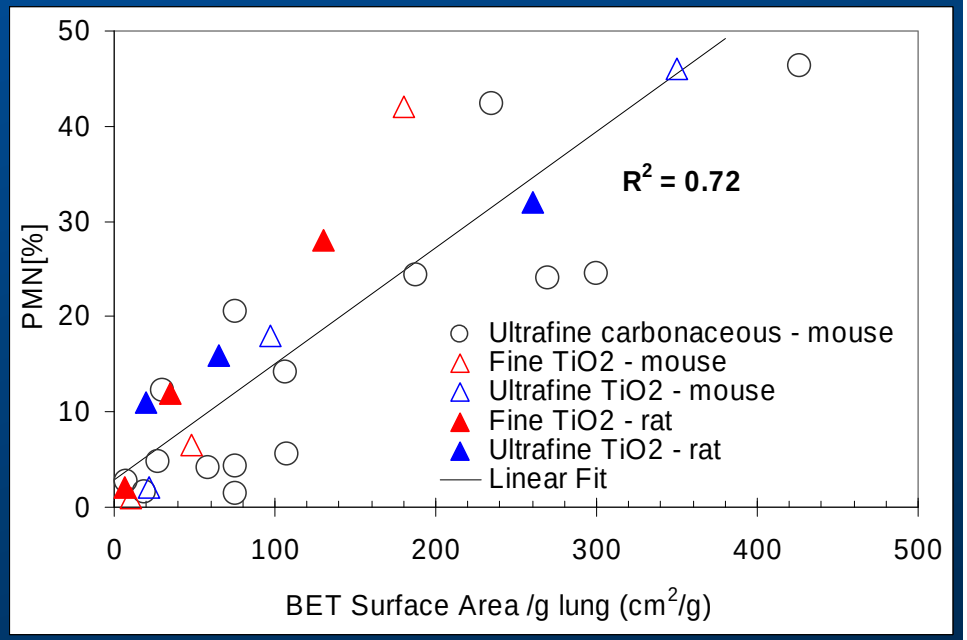
Institute for Inhalationsbiology (IHB)
Helmholtz Center Munich
German Research Center for Environmental Health

Motivation: Biology and SSA

Number



Surface



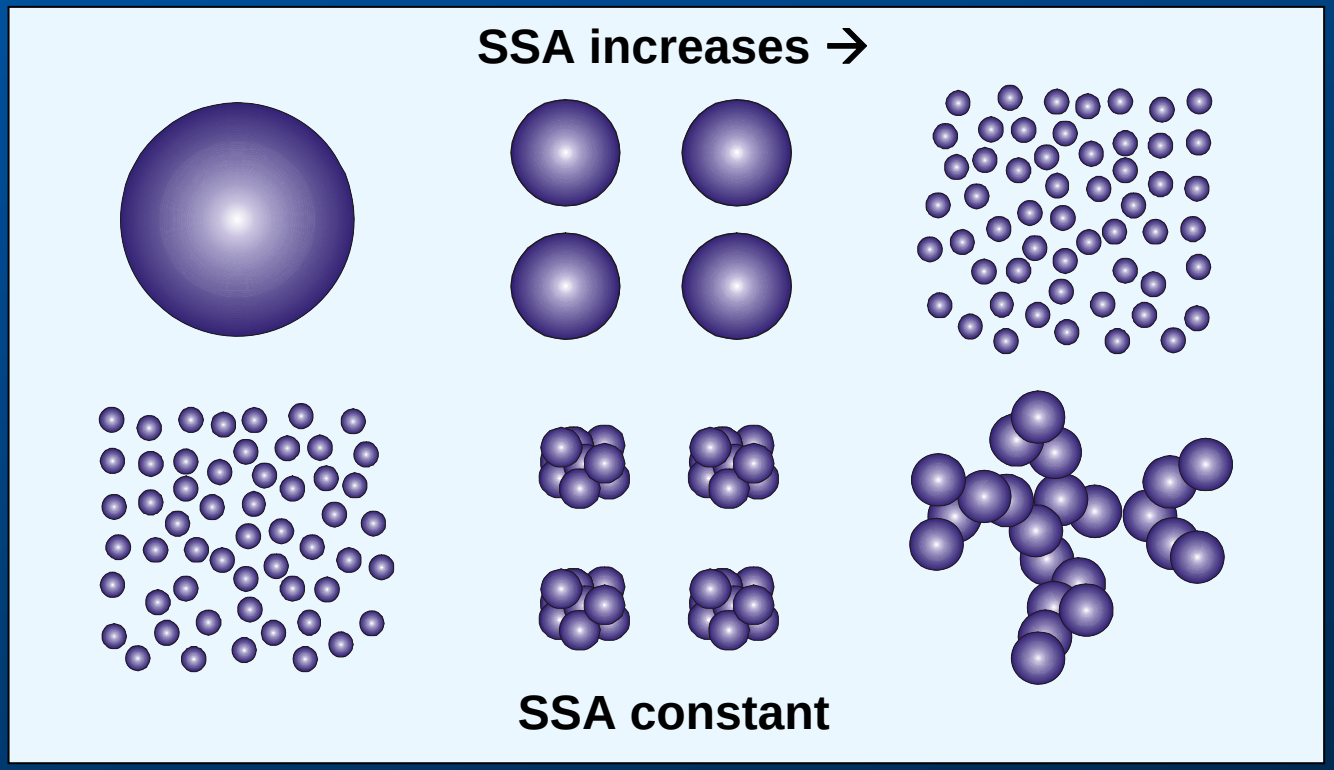
Inflammatory response to TiO_2 and C particles correlate with SSA measurements
PMN Influx measured 24h after (instillation) challange with particles

Stoeger et al., EHP 2007
Stoeger et al., EHP 2006
Oberdorster et al., EHP 2005

Definition of SSA

SSA = A / M

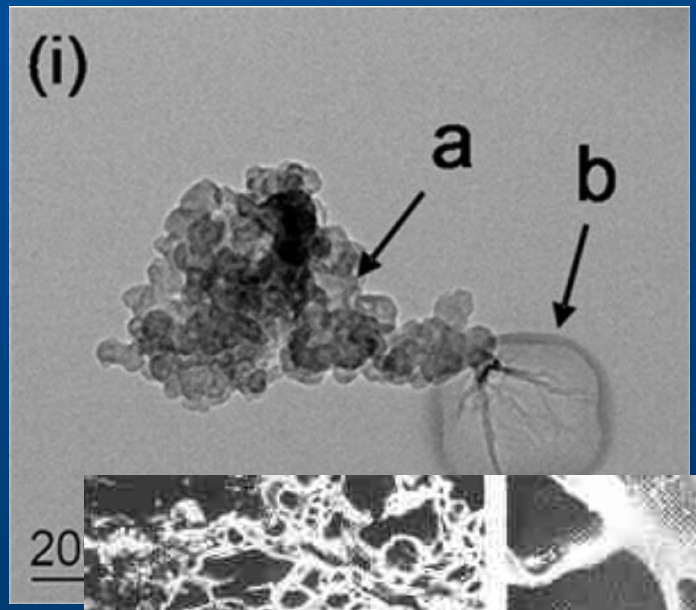
M=const



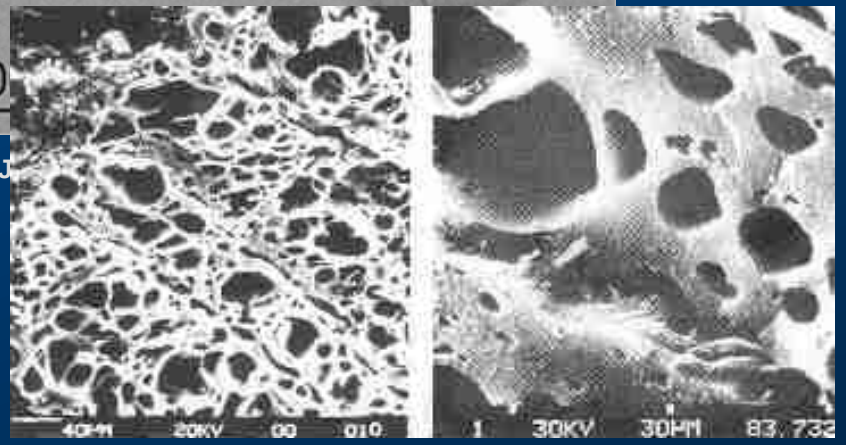
SSA sensitive to structure

SSA is sensitive to structure

- additionally to form factor, the SSA is sensitive to the material's structure
- the texture is taken into account
- techniques are well developped



K.S.J



http://www.wasser-wissen.de/abwasserlexikon/a/aktivkohle.htm

Measurement techniques

- Microscopic
- Chemical absorption of molecules
- Attachment of ions
- Physical adsorption of molecules

EMSA **(Electron microscope surface area)**

Iodine absorption, CTAB
(Cetyltrimethylammonium Bromide, withdrawn by the American Society for Testing and Materials (ASTM) in 2007)

ASA (active surface area Rogak et al., 1991)

$$ASA_m = \frac{d_{SMD}^2}{\rho d_{MMD}^3}$$

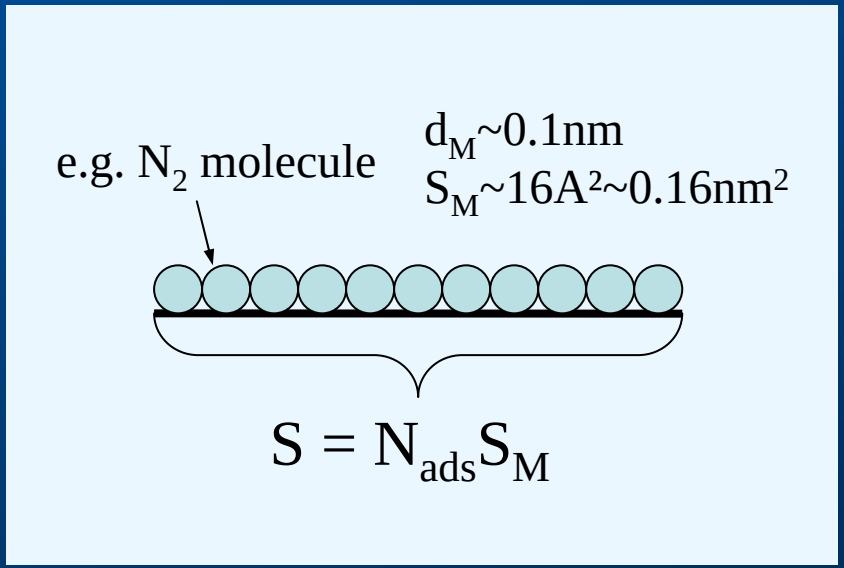
Attachment of Ions to particles<100nm is proportional to the surface area of the particles (Pandis, JAS 22(4),p.417, 1991)

Condensation methods:
Volumetric, radiometric, gas chromatographic vacuum-microbalance, piezo-gravimetric, Millican-oil-drop

Measurement principle

Methods are not new:

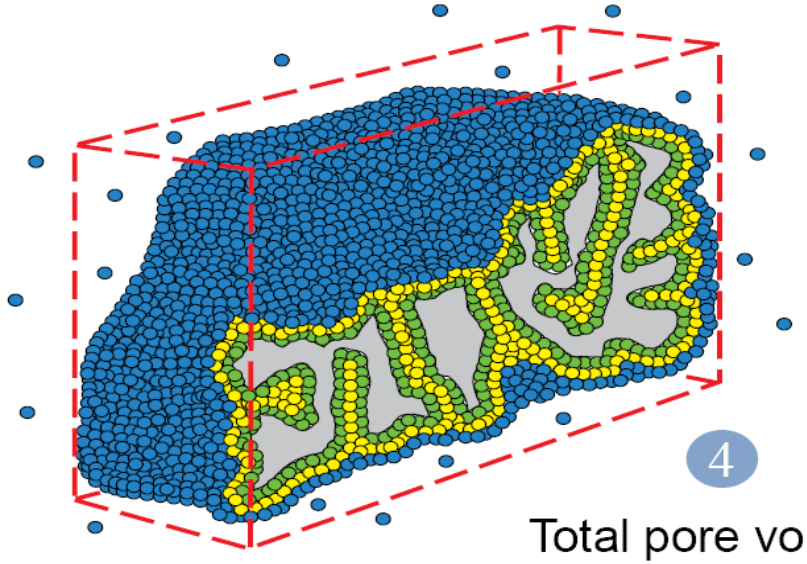
- Irving Langmuir received the Nobel prize 1932 for fundamental work in surface chemistry
- Stephen Brunauer, P.H. Emmet and Edward Teller (BET) developed their theory of interpretation of adsorption isothermes
- Adsorption Isotherme:
  T = 77K (boiling point of N_2)
  $0 < P/P_o < 1$



Brunauer et al. (1938): Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60, p. 309

Condensation of molecules

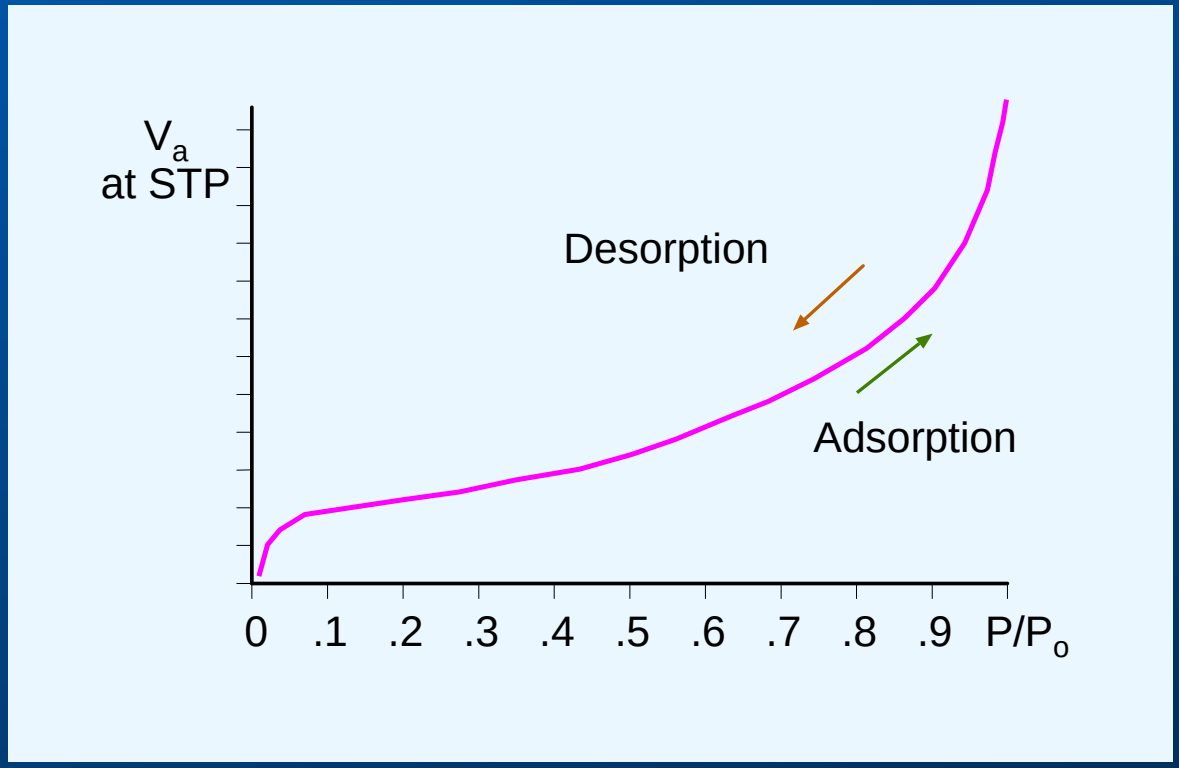
… on a particle with pores



Total pore volume filling; approximately 100% saturation.

http://www.quantachrome.com/pdf_brochures/07160.pdf

What is an isotherme?



Bulk condensation to a liquid

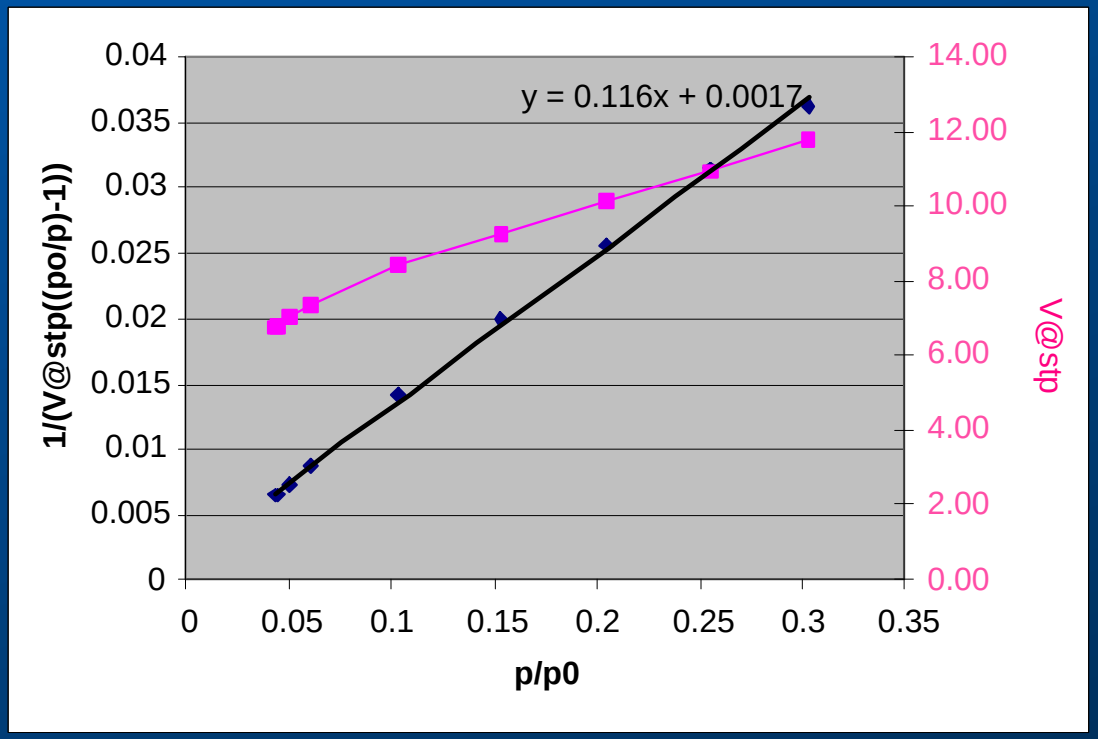
Multiple layers

Monolayer

Adsorption on most-energetic sites

Isothermal conditions (77 K)

BET equation



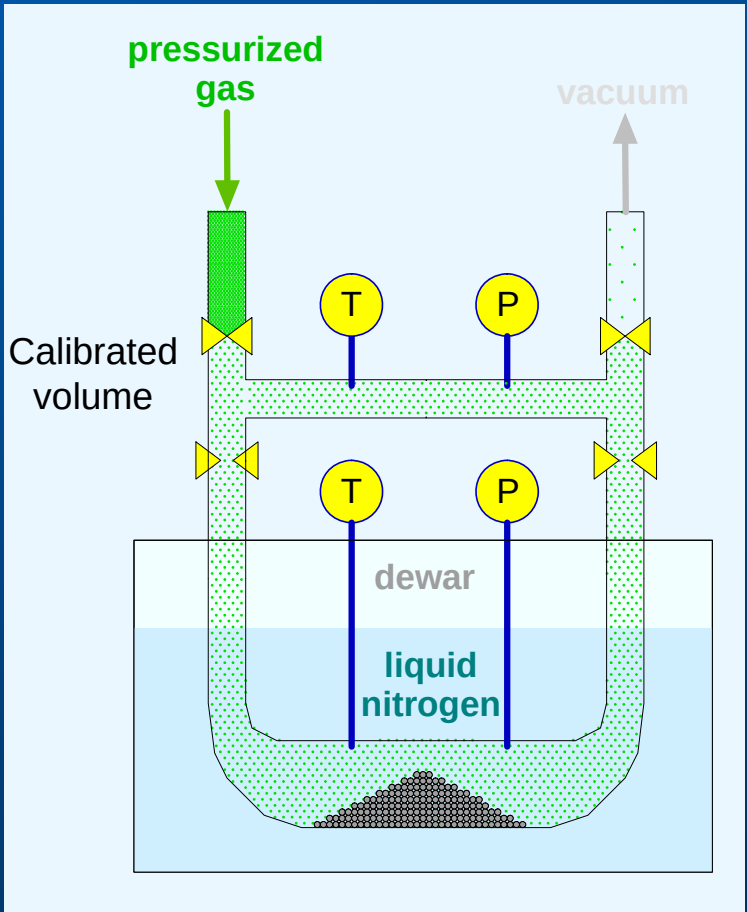
The BET equation

$$\frac{P}{v(P_o - P)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{P}{P_o}$$

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

v: adsorbed volume
v_m: volume of the mono layer
c: BET constant
E_1: Heat of adsorption Layer1
E_L: Heat of ads. Layer2 … n

Measurement setup



Volumetric method:

- Outgassing (remove H_2O, CO_2)
- Cool with liquid N_2 (constant level)
- Fill calibrated volume
- Release into sample volume
- Adsorbed volume: calculate from pressure difference

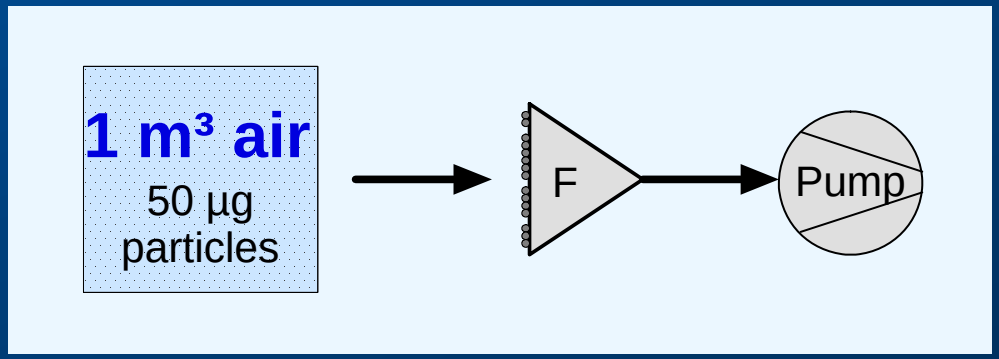
Advantages:
-Mostly glass surfaces
-Direct measurement
-Various gases (N_2, Ar, Kr, Xe)
-Robust (vibration, electrostatics, …)
-Outgassing in the same containment
-Commercially available

Disadvantages:
-Blank correction necessary
-Dead space correction necessary
-Adherent particles above N_{2liq}

The lower the mass ...

Aerosol science samples ...
... meet material science methods

- Material science: enough sample mass available (>> 100 mg)
- Aerosol science: sample mass is very very limited (<< 10 mg)



50 µg / 1.3 kg ~ 40 ppb

1 g of sample ~ 800 tons of air

1 mg of sample ~ 800 kg of air (1000 m³)

Lab: 1 mg of sample ~ 8 kg of air (10m³)

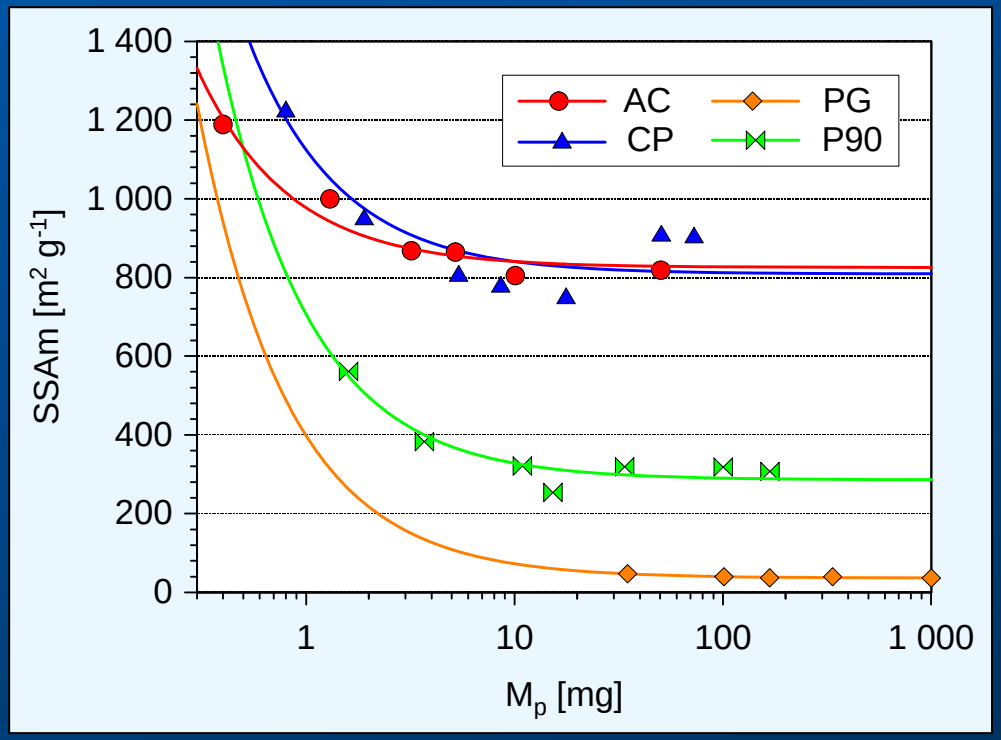
Performed experiments

- 4 carbonaceous substances of different surface area
- Produce several (~7) aliquots of each substance
- Measure all of them under optimal repeatability conditions (instrument, vial, operator, …)

Substances:

AC: activated charcoal (d_o = n.a., SSA ~ 900 m²/g)
P90 Degussa Printex 90 (d_o = 14 nm, SSA ~ 300 m²/g)
PG Degussa Printex G (d_o = 50 nm, SSA ~ 30 m²/g)
CP Palas electric spark soot (d_o = 5-10? nm, SSA = ?)

Overview of all data sets



- wide variation of SSA
- All data sets show a bias for low mass samples

Fit equations

$$SSA_m = \frac{A_d + A_p}{M_p} = \frac{A_d}{M_p} + SSA_o$$

equ (1)

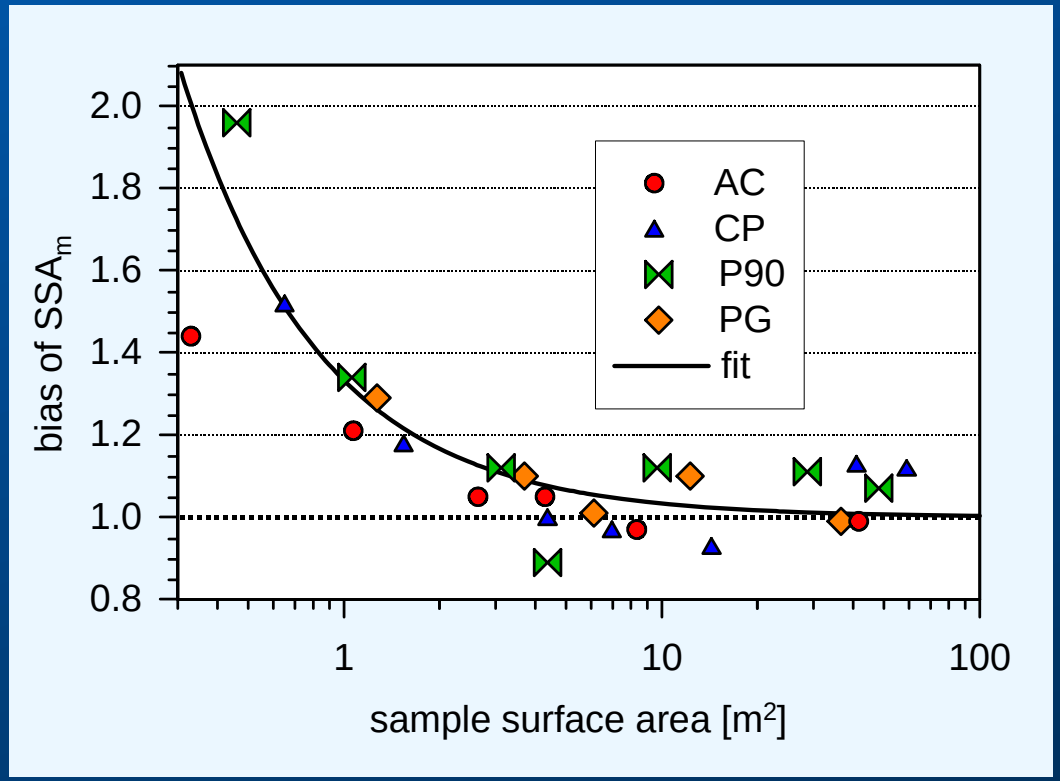
$$\frac{SSA_m}{SSA_o} = \frac{A_d}{A_p} + 1$$

equ (2)

SSA_m	measured SSA
A_d	unaccounted apparent surface area
A_p	surface area of particles
M_p	mass of particulates
SSA_o	true specific surface area of the particles

- All corrections are applied
- Working hypothesis: unaccounted apparent surface area NOT from particle sample
- Normalization shows the relation to be SUBSTANCE independent
- limiting cases:
  Ad → 0
  Ap → 0

And applies it to the data sets



	AC	CP	P90	PG
SSA_s [m²/g]	1000	n.a.	300	30
SSA_o [m²/g]	826	809	286	36.5
A_d [m²]	0.152	0.316	0.421	0.362
R	0.98	0.89	0.95	0.93
$M_{p,min}$ [mg]	4.0	4.1	11.5	90

Fit the equation to ALL data sets

$A_d = 0.267$

$R = 0.80$

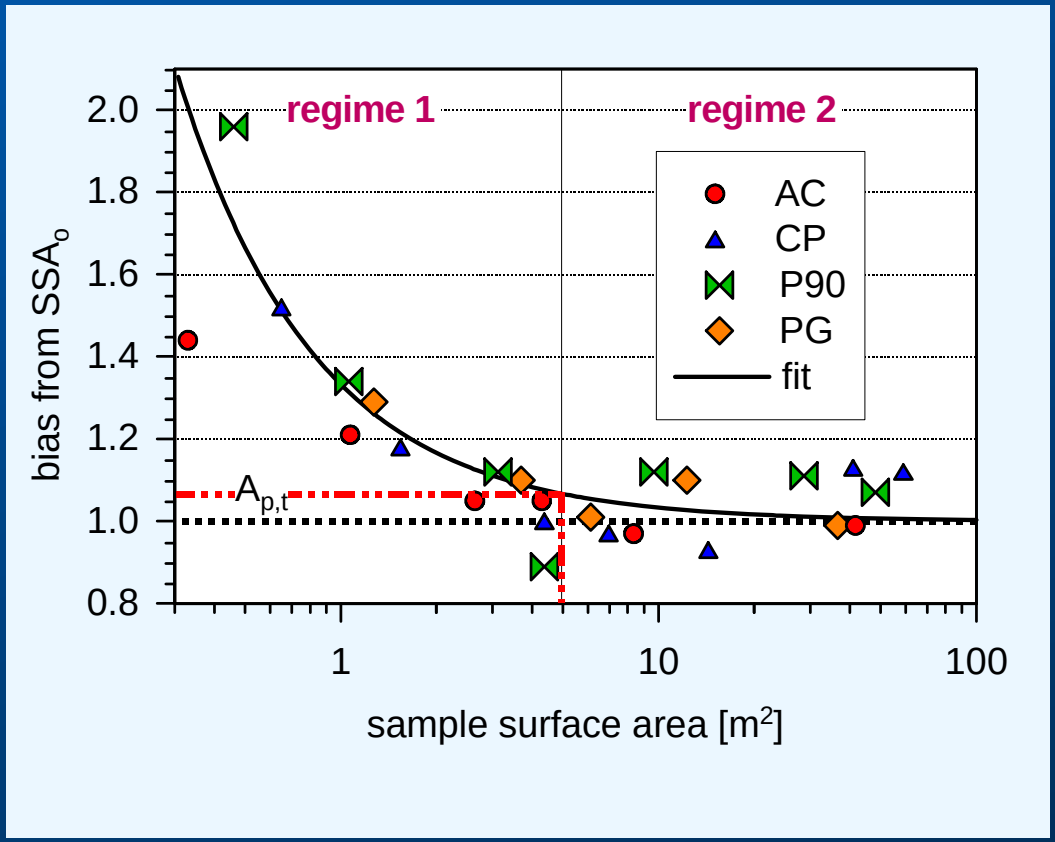
Findings

- Low sample mass bias is consistent with an unaccounted instrument surface area
- A_d is ~ constant within measurement error → cannot explained by impurities in the sampling vial

Possible explanations:

- limited accuracy of blank?
- dead space correction?
- temperature stability?

The mass threshold



- Define 2 regimes by fit line:
- 7.5% is the instrument's s.d.
- Threshold (7.5%) ist 5m²

Conclusions

- Each instrument has to be calibrated
  for low sample mass (determine A_d) by an additional calibration step
  - Determine A_d for low sample mass
  - Repeat Calibration if new blank correction is applied

- A threshold surface area of 5 m²
  is found for our instrument

Take home message

- The BET-SSA is expected to become more important because it correlates well with biological endpoints
- However: corrections for low-sample-mass artifacts have to be applied!

Thank you for your attention

Thanks to

Gabi Schumann,
for particle preparation

Dipl. Ing. Franz-Xaver Hecht,
Technical University of Munich
for BET measurements