**Eurokin Workshop – February 18th, 2015**
**Milano, Italy**

# Analysis of the nitrogen adsorption technique to characterize porous materials

## Error analysis guides the way

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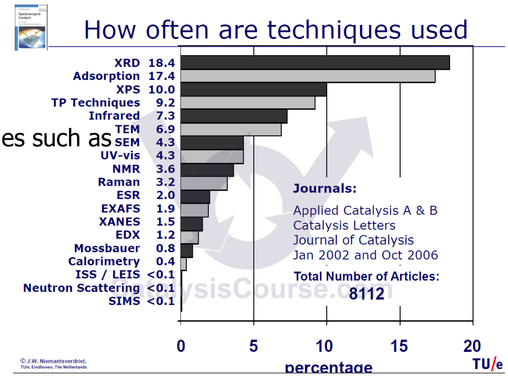
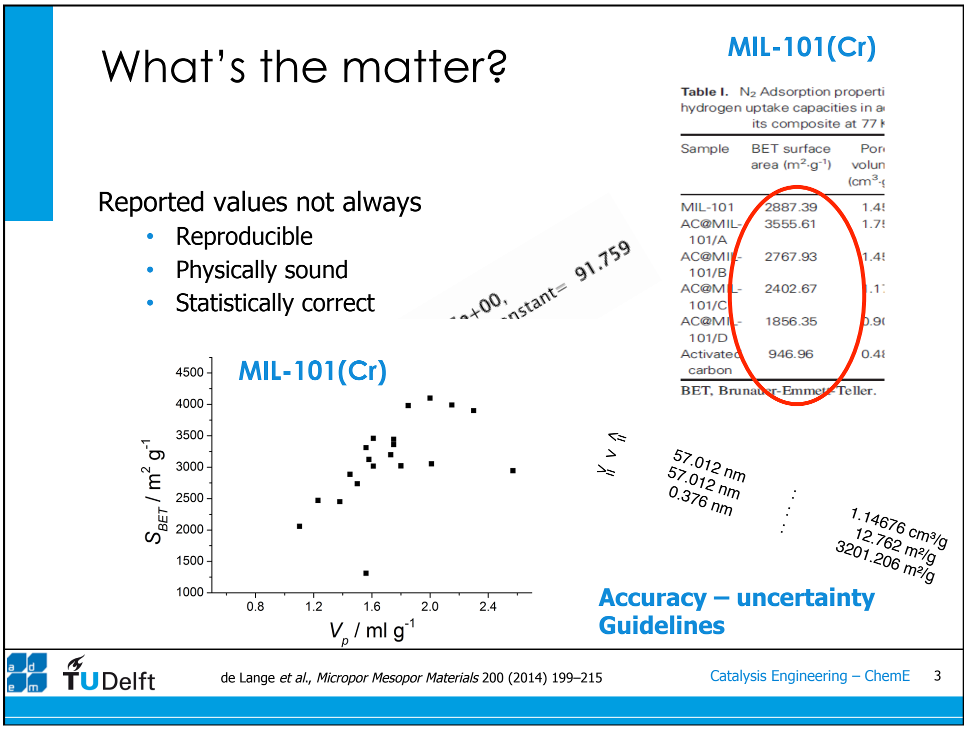
# Introduction

## Adsorptive characterization $N_2$ @ 77 K

- One of most used tools for characterization of
  - Catalysts
  - Porous adsorbents
- Physical adsorption yields quantities such as
  - Pore volume
  - Specific surface area
  - Pore size distribution



http://www.catalysiscourse.com/



# What's the matter?

Reported values not always

- Reproducible
- Physically sound
- Statistically correct

**MIL-101(Cr)**

Table I. $N_2$ Adsorption properti
hydrogen uptake capacities in a
its composite at 77

| Sample | BET surface area ($m^2 \cdot g^{-1}$) | Por volun ($cm^3 \cdot$ |
|---|---|---|
| MIL-101 | 2887.39 | 1.4 |
| AC@MIL-101/A | 3555.61 | 1.7 |
| AC@MIL-101/B | 2767.93 | 1.4 |
| AC@MIL-101/C | 2402.67 | .1 |
| AC@MIL-101/D | 1856.35 | 0.9 |
| Activated carbon | 946.96 | 0.4 |

BET, Brunauer-Emmett-Teller.

**Accuracy – uncertainty**
**Guidelines**

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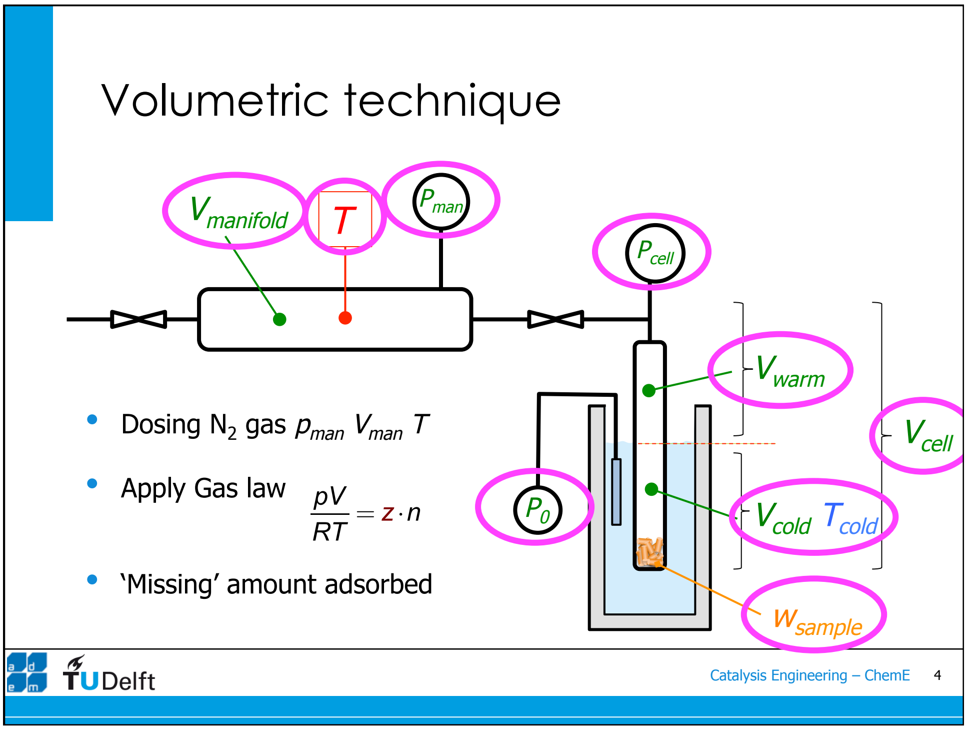


# Volumetric technique

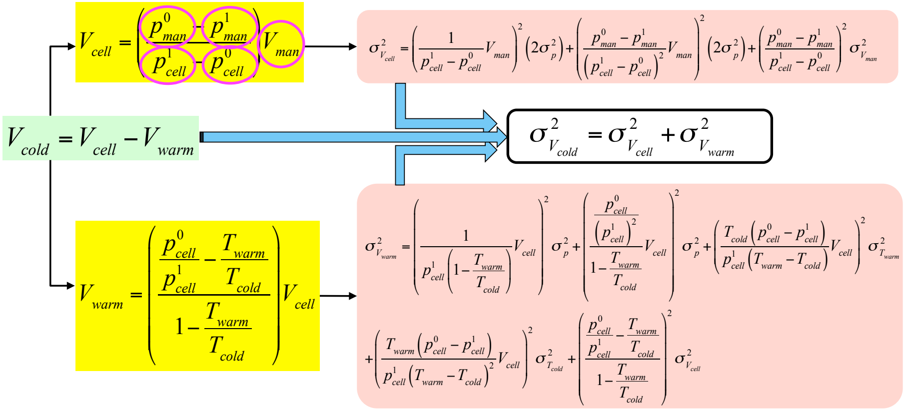
- Dosing $N_2$ gas $p_{man}$ $V_{man}$ $T$
- Apply Gas law $\frac{pV}{RT} = z \cdot n$
- 'Missing' amount adsorbed

# Error propagation analysis

$$\sigma_y^2 = \sum\left(\frac{\partial y}{\partial x_i}\right)^2 \sigma_{x_i}^2$$

e.g. see J.R. Taylor

- Volumes determination



$$V_{cell} = \left(\frac{p_{man}^0 - p_{man}^1}{p_{cell}^1 - p_{cell}^0}\right) V_{man}$$

$$\sigma_{V_{cell}}^2 = \left(\frac{1}{p_{cell}^1 - p_{cell}^0} V_{man}\right)^2 \left(2\sigma_p^2\right) + \left(\frac{p_{man}^0 - p_{man}^1}{\left(p_{cell}^1 - p_{cell}^0\right)^2} V_{man}\right)^2 \left(2\sigma_p^2\right) + \left(\frac{p_{man}^0 - p_{man}^1}{p_{cell}^1 - p_{cell}^0}\right)^2 \sigma_{V_{man}}^2$$

$$V_{cold} = V_{cell} - V_{warm}$$

$$\boxed{\sigma_{V_{cold}}^2 = \sigma_{V_{cell}}^2 + \sigma_{V_{warm}}^2}$$

$$V_{warm} = \left(\frac{\frac{p_{cell}^0}{p_{cell}^1} - \frac{T_{warm}}{T_{cold}}}{1 - \frac{T_{warm}}{T_{cold}}}\right) V_{cell}$$

$$\sigma_{V_{warm}}^2 = \left(\frac{1}{p_{cell}^1\left(1 - \frac{T_{warm}}{T_{cold}}\right)} V_{cell}\right)^2 \sigma_p^2 + \left(\frac{\frac{p_{cell}^0}{\left(p_{cell}^1\right)^2}}{1 - \frac{T_{warm}}{T_{cold}}} V_{cell}\right)^2 \sigma_p^2 + \left(\frac{T_{cold}\left(p_{cell}^0 - p_{cell}^1\right)}{p_{cell}^1\left(T_{warm} - T_{cold}\right)} V_{cell}\right)^2 \sigma_{T_{warm}}^2$$
$$+ \left(\frac{T_{warm}\left(p_{cell}^0 - p_{cell}^1\right)}{p_{cell}^1\left(T_{warm} - T_{cold}\right)^2} V_{cell}\right)^2 \sigma_{T_{cold}}^2 + \left(\frac{\frac{p_{cell}^0}{p_{cell}^1} - \frac{T_{warm}}{T_{cold}}}{1 - \frac{T_{warm}}{T_{cold}}}\right)^2 \sigma_{V_{cell}}^2$$

J.R. Taylor, An introduction to Error Analysis, 2nd ed., University Science Books, 1997.

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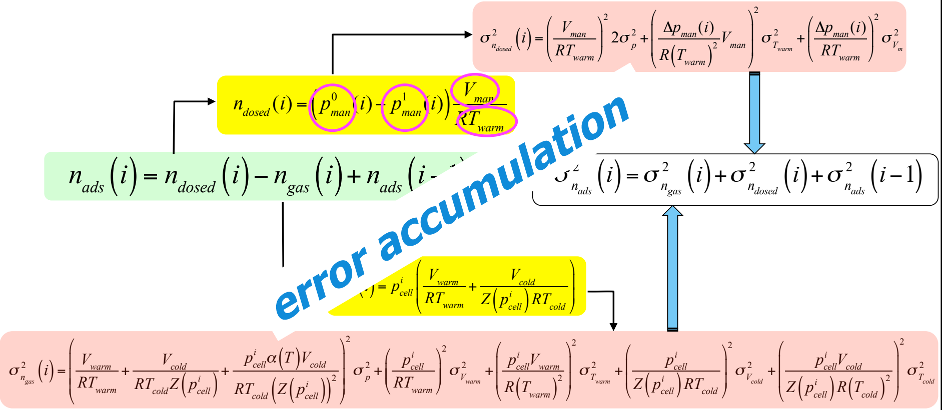
# Error propagation analysis

$$\sigma_y^2 = \sum\left(\frac{\partial y}{\partial x_i}\right)^2 \sigma_{x_i}^2$$

- e.g. see J.R. Taylor



$$\sigma_{n_{dosed}}^2(i) = \left(\frac{V_{man}}{RT_{warm}}\right)^2 2\sigma_p^2 + \left(\frac{\Delta p_{man}(i)}{R\left(T_{warm}\right)^2} V_{man}\right)^2 \sigma_{T_{warm}}^2 + \left(\frac{\Delta p_{man}(i)}{RT_{warm}}\right)^2 \sigma_{V_m}^2$$

$$n_{dosed}(i) = \left(p_{man}^0(i) - p_{man}^1(i)\right)\frac{V_{man}}{RT_{warm}}$$

$$n_{ads}(i) = n_{dosed}(i) - n_{gas}(i) + n_{ads}(i -$$

$$\sigma_{n_{ads}}^2(i) = \sigma_{n_{gas}}^2(i) + \sigma_{n_{dosed}}^2(i) + \sigma_{n_{ads}}^2(i-1)$$

error accumulation

$$(i) = p_{cell}^i\left(\frac{V_{warm}}{RT_{warm}} + \frac{V_{cold}}{Z\left(p_{cell}^i\right)RT_{cold}}\right)$$

$$\sigma_{n_{gas}}^2(i) = \left(\frac{V_{warm}}{RT_{warm}} + \frac{V_{cold}}{RT_{cold}Z\left(p_{cell}^i\right)} + \frac{p_{cell}^i\alpha(T)V_{cold}}{RT_{cold}\left(Z\left(p_{cell}^i\right)\right)^2}\right)^2 \sigma_p^2 + \left(\frac{p_{cell}^i}{RT_{warm}}\right)^2 \sigma_{V_{warm}}^2 + \left(\frac{p_{cell}^i V_{warm}}{R\left(T_{warm}\right)^2}\right)^2 \sigma_{T_{warm}}^2 + \left(\frac{p_{cell}^i}{Z\left(p_{cell}^i\right)RT_{cold}}\right)^2 \sigma_{V_{cold}}^2 + \left(\frac{p_{cell}^i V_{cold}}{Z\left(p_{cell}^i\right)R\left(T_{cold}\right)^2}\right)^2 \sigma_{T_{cold}}^2$$

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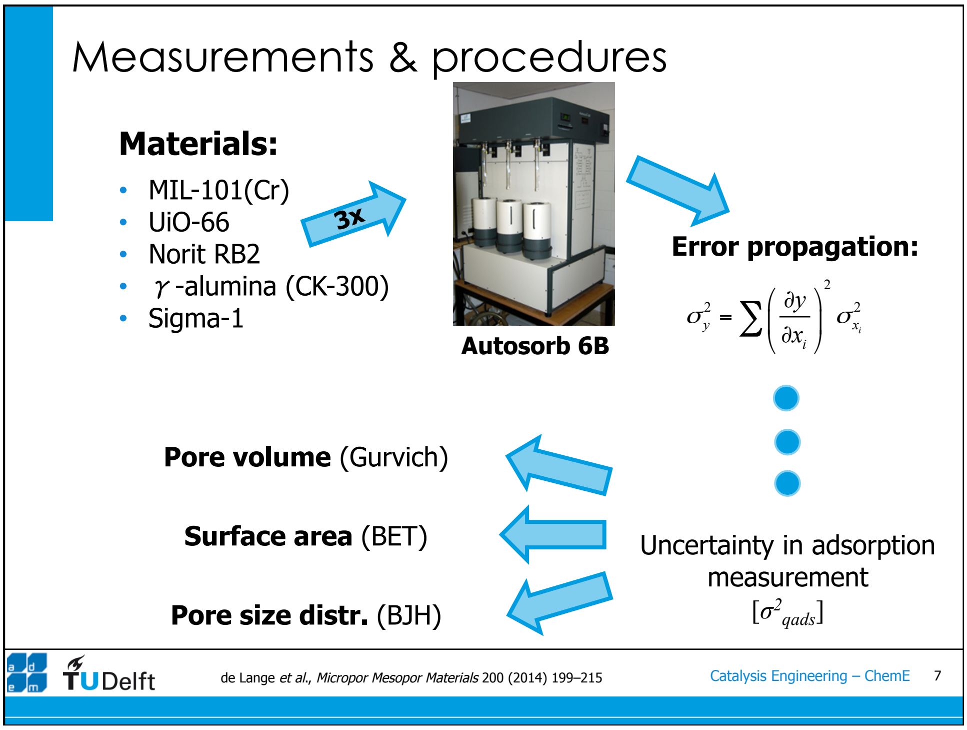

# Measurements & procedures

**Materials:**

- MIL-101(Cr)
- UiO-66
- Norit RB2
- $\gamma$-alumina (CK-300)
- Sigma-1

**Autosorb 6B**

**Error propagation:**

$$\sigma_y^2 = \sum\left(\frac{\partial y}{\partial x_i}\right)^2 \sigma_{x_i}^2$$

Uncertainty in adsorption measurement

$[\sigma^2{}_{qads}]$

**Pore volume** (Gurvich)

**Surface area** (BET)

**Pore size distr.** (BJH)

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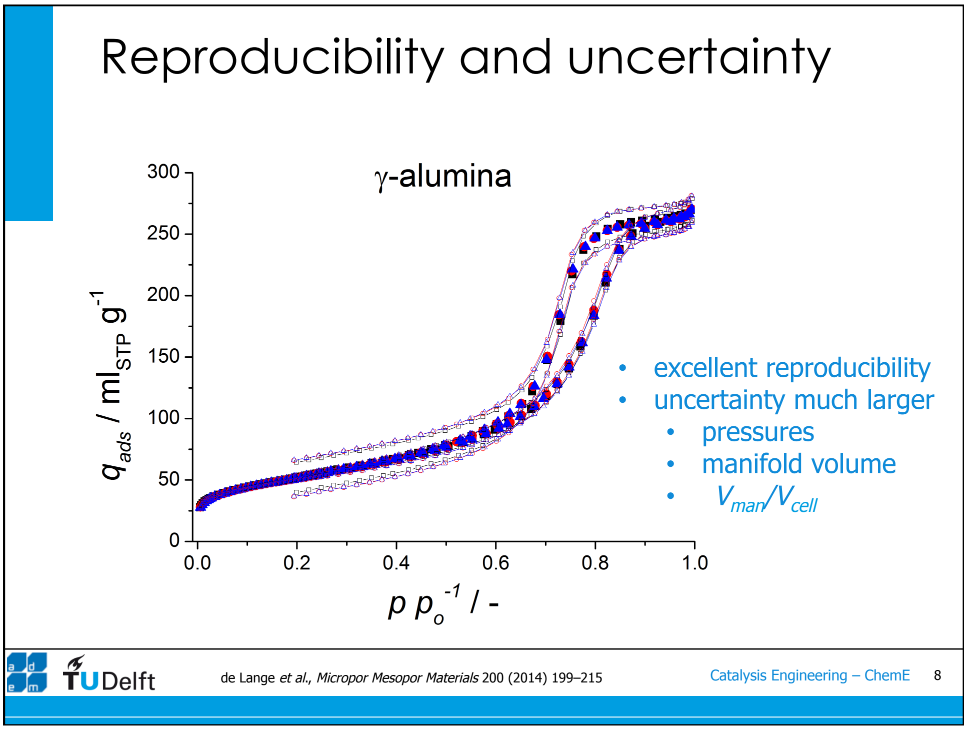

# Reproducibility and uncertainty

- excellent reproducibility
- uncertainty much larger
  - pressures
  - manifold volume
  - $V_{man}/V_{cell}$

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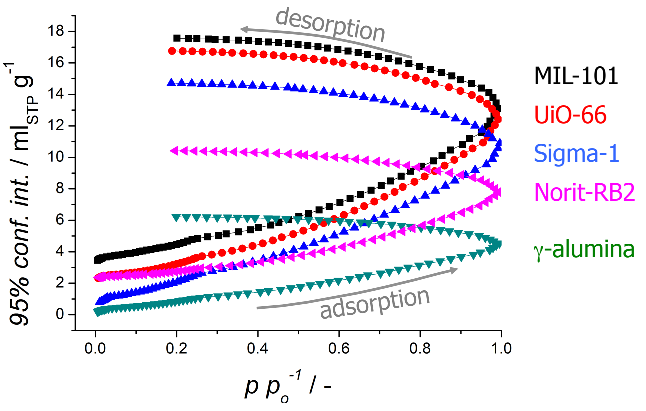
# Uncertainties - 95% confidence interval

(single dose assumption)



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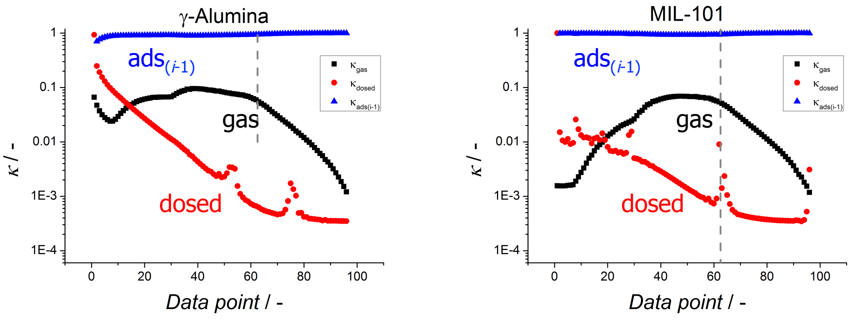
# Error breakdown

$$n_{ads}(i) = n_{dosed}(i) - n_{gas}(i) + n_{ads}(i-1)$$



Variance (normalized) of gas, dose, adsorbed ($i$-1)
Single dose assumption

Variance adsorbed amount previous step largest

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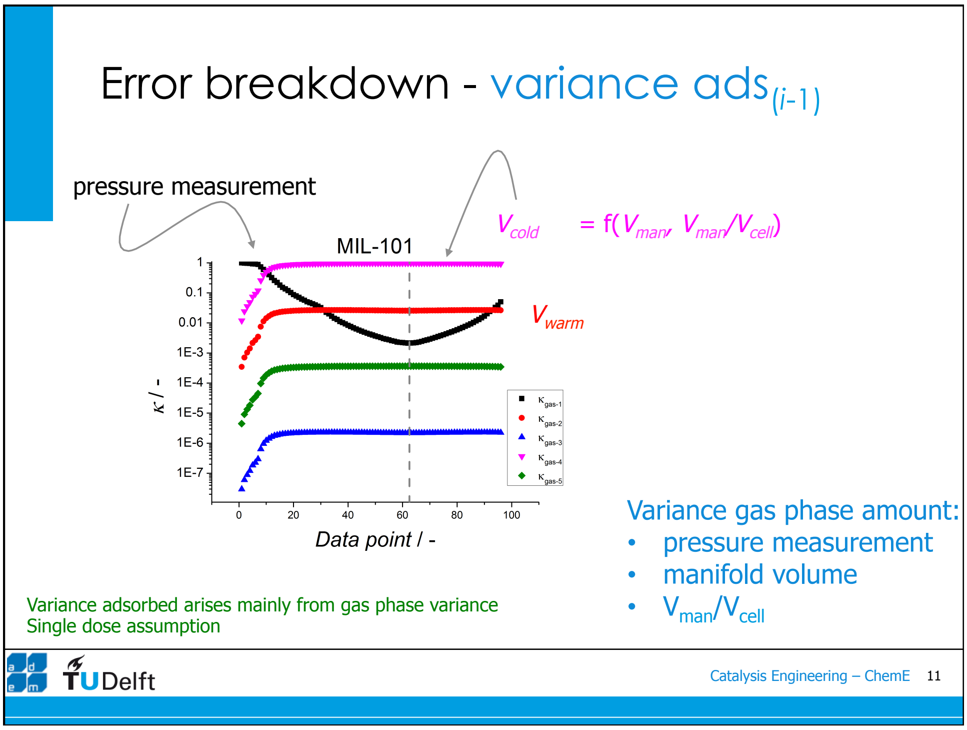


# Error breakdown - variance ads$_{(i-1)}$

pressure measurement

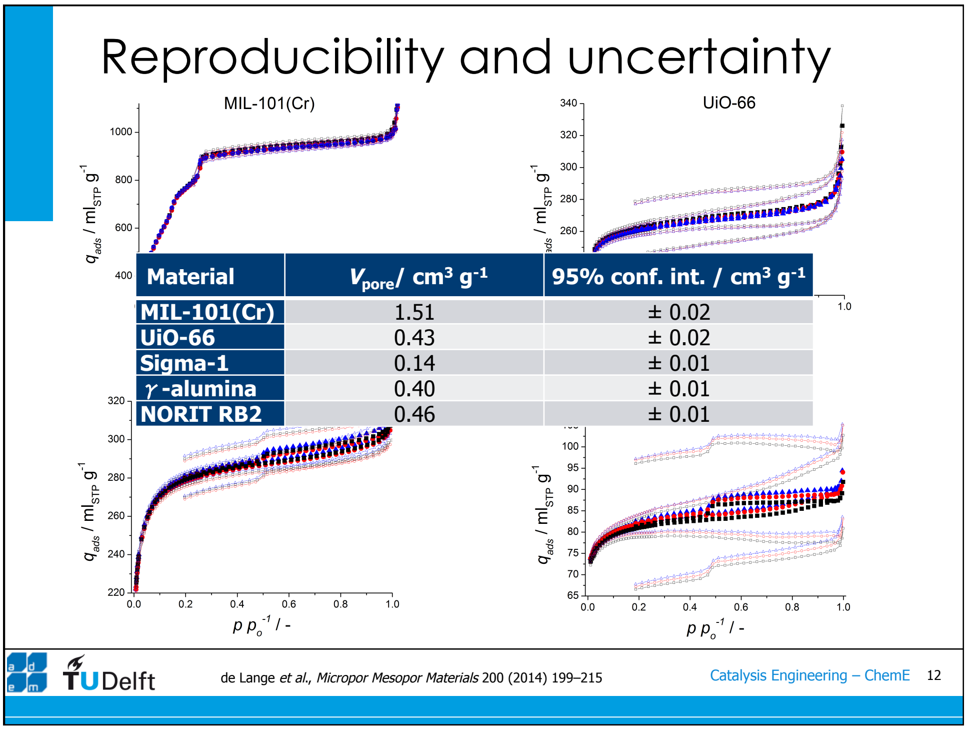
$V_{cold}$ $= f(V_{man}, V_{man}/V_{cell})$

$V_{warm}$

Variance gas phase amount:

- pressure measurement
- manifold volume
- $V_{man}/V_{cell}$

Variance adsorbed arises mainly from gas phase variance
Single dose assumption



# Reproducibility and uncertainty

| Material | $V_{pore}$/ cm³ g⁻¹ | 95% conf. int. / cm³ g⁻¹ |
|---|---|---|
| **MIL-101(Cr)** | 1.51 | ± 0.02 |
| **UiO-66** | 0.43 | ± 0.02 |
| **Sigma-1** | 0.14 | ± 0.01 |
| **γ-alumina** | 0.40 | ± 0.01 |
| **NORIT RB2** | 0.46 | ± 0.01 |

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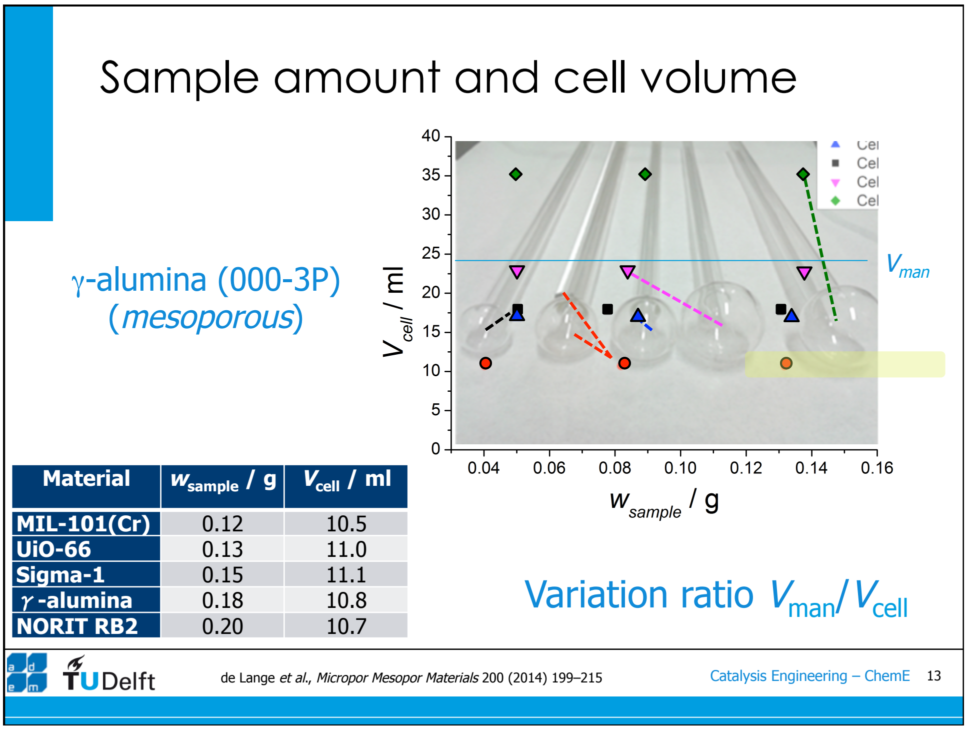

# Sample amount and cell volume

γ-alumina (000-3P)
(*mesoporous*)

| Material | $w_{sample}$ / g | $V_{cell}$ / ml |
|---|---|---|
| **MIL-101(Cr)** | 0.12 | 10.5 |
| **UiO-66** | 0.13 | 11.0 |
| **Sigma-1** | 0.15 | 11.1 |
| **γ-alumina** | 0.18 | 10.8 |
| **NORIT RB2** | 0.20 | 10.7 |

Variation ratio $V_{man}/V_{cell}$

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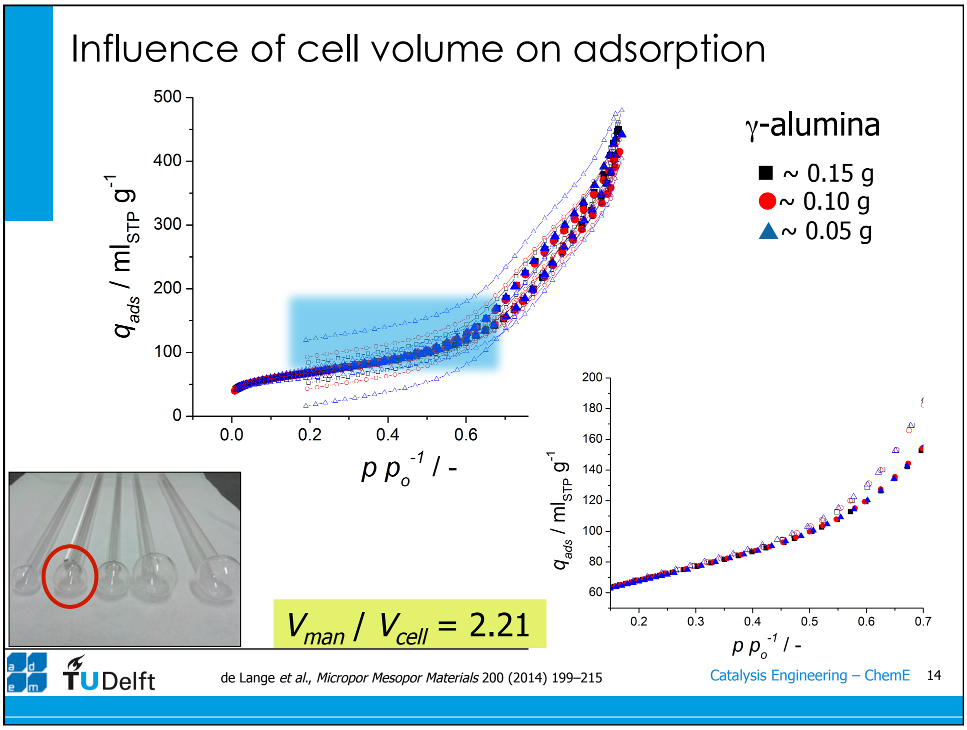

# Influence of cell volume on adsorption

$V_{man}$ / $V_{cell}$ = 2.21

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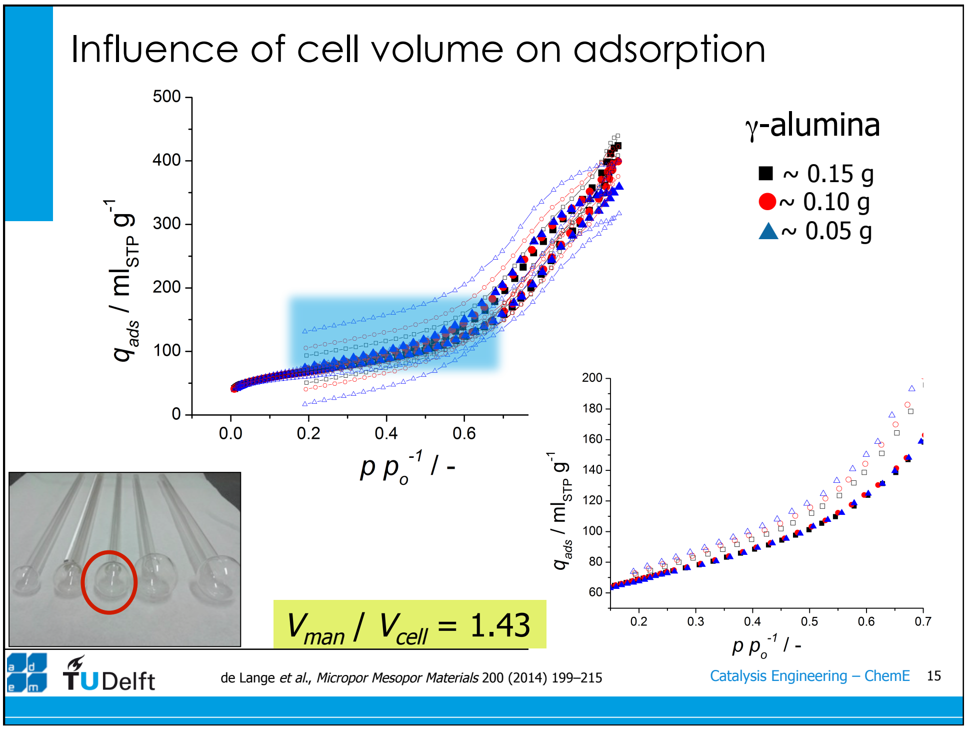

# Influence of cell volume on adsorption

γ-alumina

■ ~ 0.15 g
● ~ 0.10 g
▲ ~ 0.05 g

$V_{man}$ / $V_{cell}$ = 1.43

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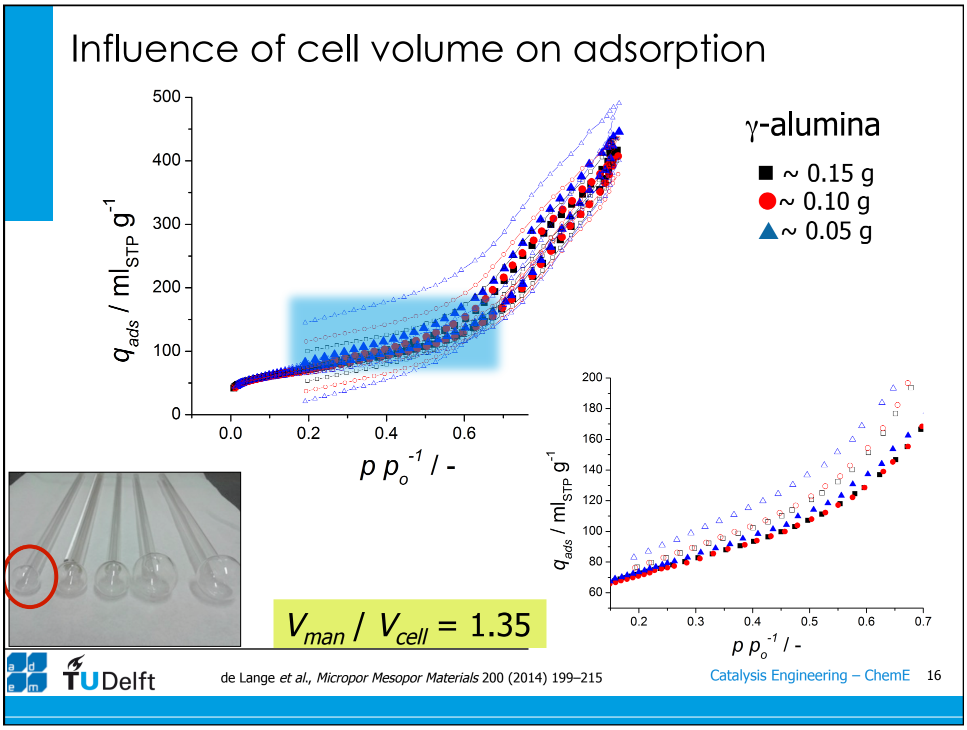

# Influence of cell volume on adsorption

γ-alumina

■ ~ 0.15 g
● ~ 0.10 g
▲ ~ 0.05 g

$V_{man}$ / $V_{cell}$ = 1.35

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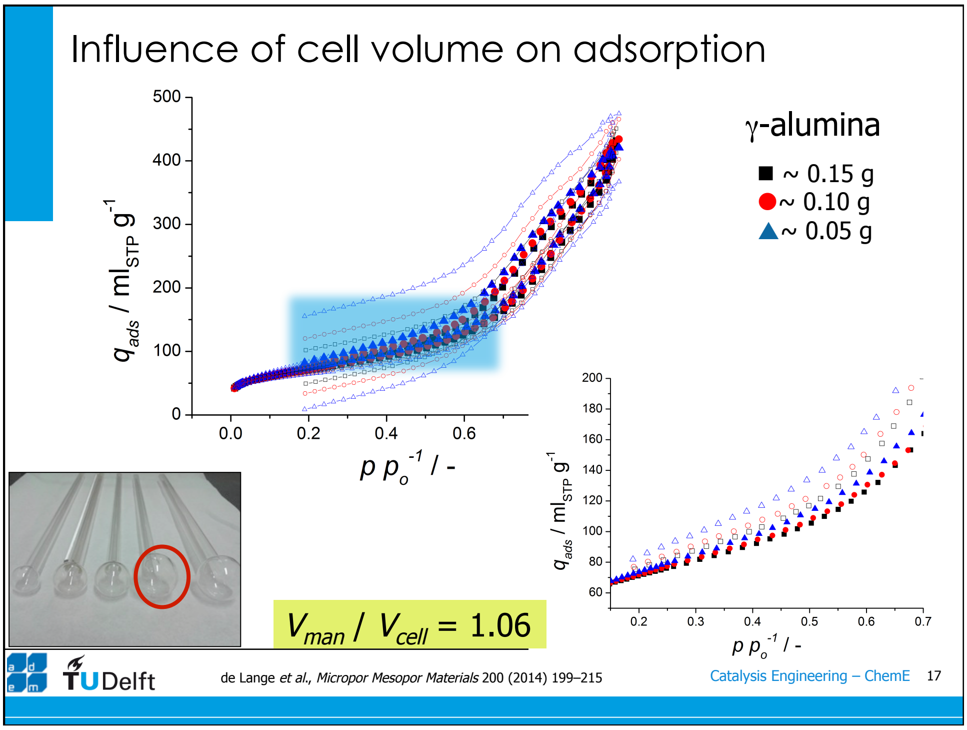

# Influence of cell volume on adsorption

γ-alumina

■ ~ 0.15 g
● ~ 0.10 g
▲ ~ 0.05 g

$V_{man}$ / $V_{cell}$ = 1.06

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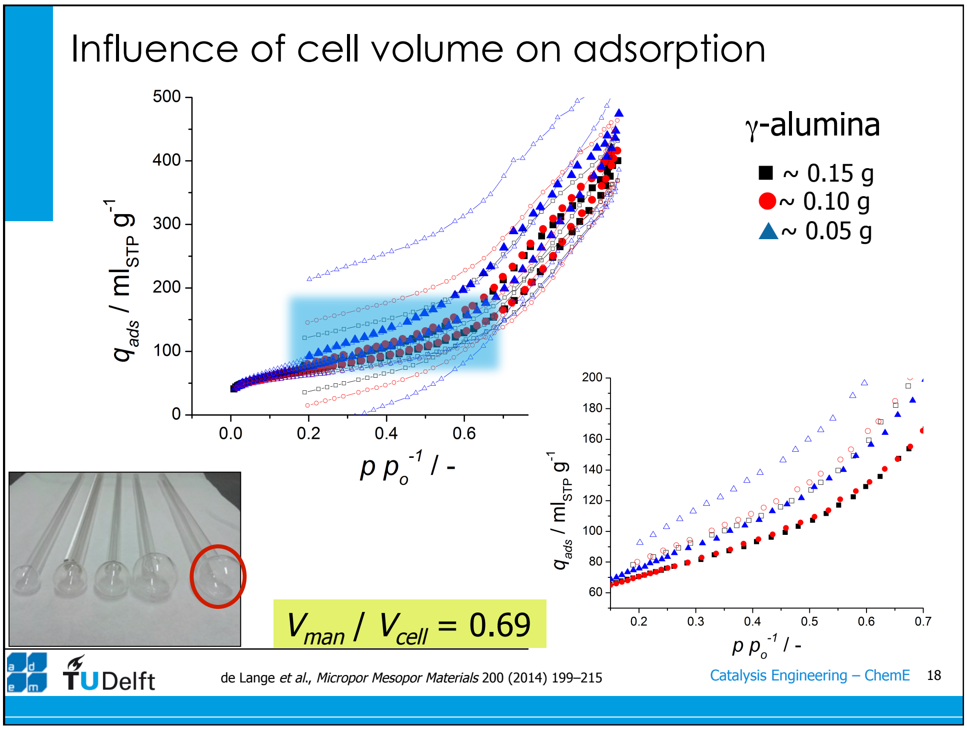

# Influence of cell volume on adsorption

γ-alumina

■ ~ 0.15 g
● ~ 0.10 g
▲ ~ 0.05 g

$V_{man}$ / $V_{cell}$ = 0.69

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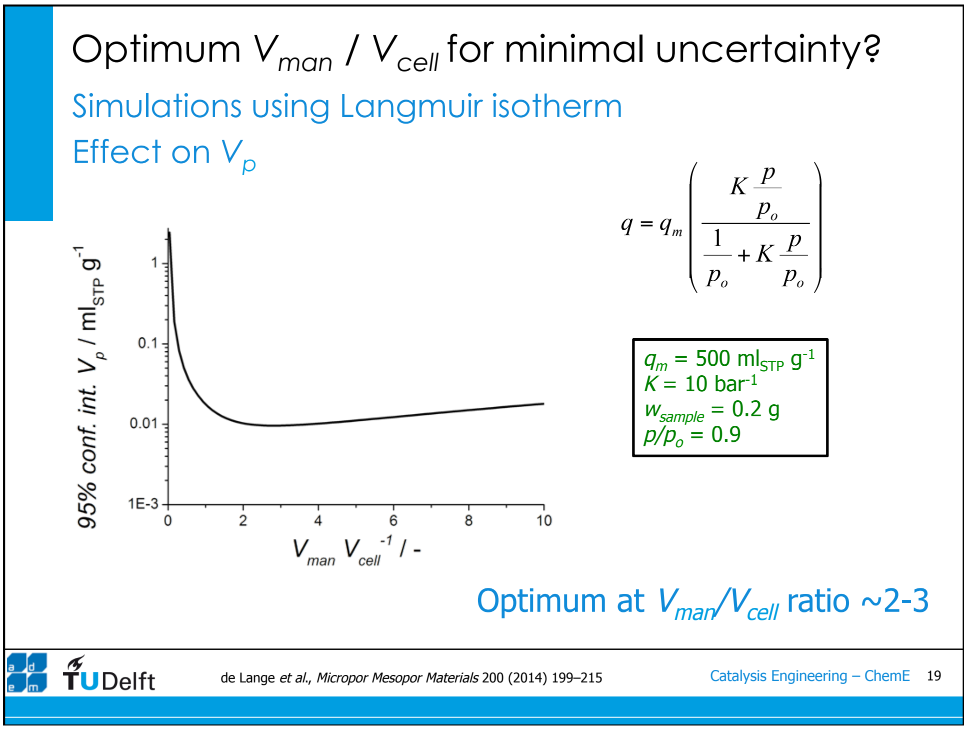


## Optimum $V_{man}$ / $V_{cell}$ for minimal uncertainty?

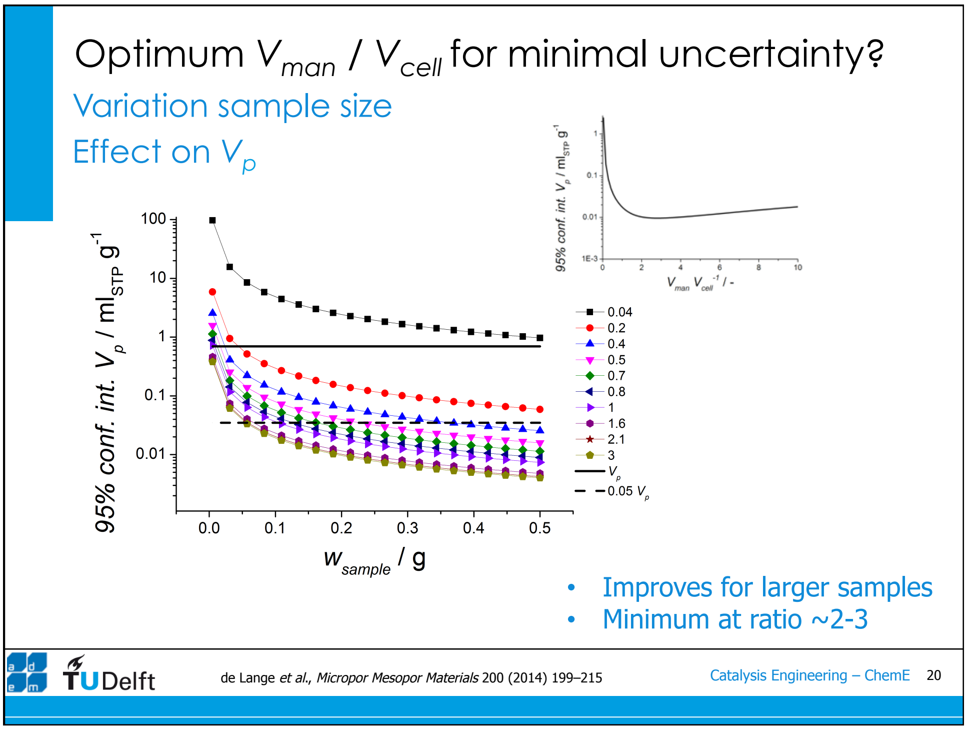
Simulations using Langmuir isotherm

Effect on $V_p$

$$q = q_m \left( \frac{K\frac{p}{p_o}}{\frac{1}{p_o}+K\frac{p}{p_o}} \right)$$

$q_m$ = 500 $ml_{STP}$ $g^{-1}$
$K$ = 10 $bar^{-1}$
$w_{sample}$ = 0.2 g
$p/p_o$ = 0.9

Optimum at $V_{man}/V_{cell}$ ratio ~2-3



## Optimum $V_{man}$ / $V_{cell}$ for minimal uncertainty?

Variation sample size

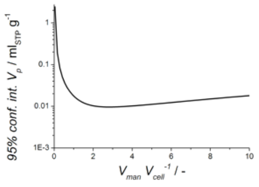
Effect on $V_p$

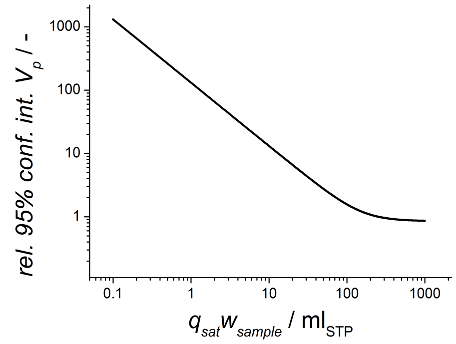
- Improves for larger samples
- Minimum at ratio ~2-3

# Optimum $V_{man}$ / $V_{cell}$ for minimal uncertainty?

## Variation sample mass

## Effect on $V_p$





Optimum reached at sorbed amounts of ~100 $ml_{STP}$

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# Observations – Variation sample mass and cell volume

## Effect on $V_p$

- Optimum ratio $V_{man}/V_{cel}$ ~2-3
- Artificial hysteresis introduced for
  - Larger cell volume
  - Lower sample mass (+ higher inaccuracy)
- Sorbed capacity ~ 100 ml

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# BET model and surface area

$$q = q_m \left( \frac{C\left(\frac{p}{p_o}\right)}{\left\{1-\frac{p}{p_o}+C\left(\frac{p}{p_o}\right)\right\}\cdot\left\{1-\left(\frac{p}{p_o}\right)\right\}} \right)$$

$$\frac{\frac{p}{p_o}}{q\left(1-\frac{p}{p_o}\right)} = \left(\frac{1}{Cq}\right)+\left(\frac{C-1}{Cq}\right)\cdot\left(\frac{p}{p}\right)$$

$$q_m = \left(\frac{1}{I+S}\right),$$

- Traditionally equation is **linearized**:
  - Linear least squares fitting procedure
  - Quality visible "by the eye"
  - Applicable somewhere between:
    - 0.05–0.35 $p/p_o$ (B,E & T)
    - 0.05-0.30 $p/p_o$ (IUPAC)

Important:
*-Values highly determined by fitting strategy-*
- $C > 0$
- Choose right $p/p_o$ window

$$S_{BET} = \frac{q_m \rho_{STP}^{vap.} N_A A_{CS}}{M_{N_2}}$$

Determination limits $p/p_0$
Direct fitting (non-linear parameter estimation)

**Brunauer, Emmett & Teller, 1938**

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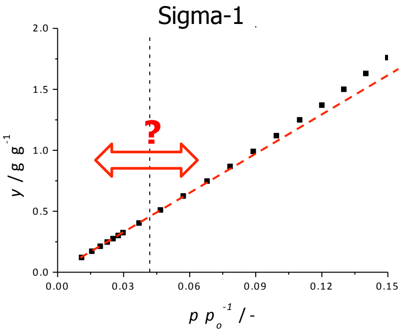
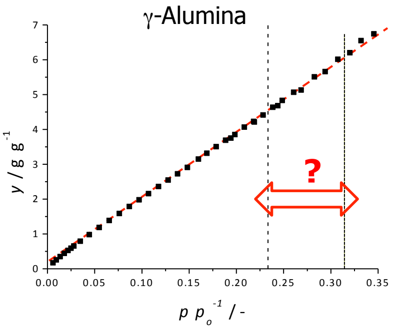
# Linearized BET

- Linearization changes error distribution
- What tells your 'eye'?





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