Absolute Calibration of SAS Data

{ By John Barker for SAS2009, 9/16/2009 }

1. **Calibration of q**
   a. q-standard samples: (Ag-behenate, Guinier Radius (R_G)
   β. λ-standards: (k-absorption edges, TOF)
2. **Calibration of I(q)**
   a. Standard samples
   b. Measure beam current directly
3. **Corrections**
   a. Smearing, multiple scattering, detector dead time

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Bragg Scattering from large d-spacing Polycrystals: **Ag-Behenate**

$$q_{001} = \frac{2\pi}{d} = 0.1076 A^{-1}$$

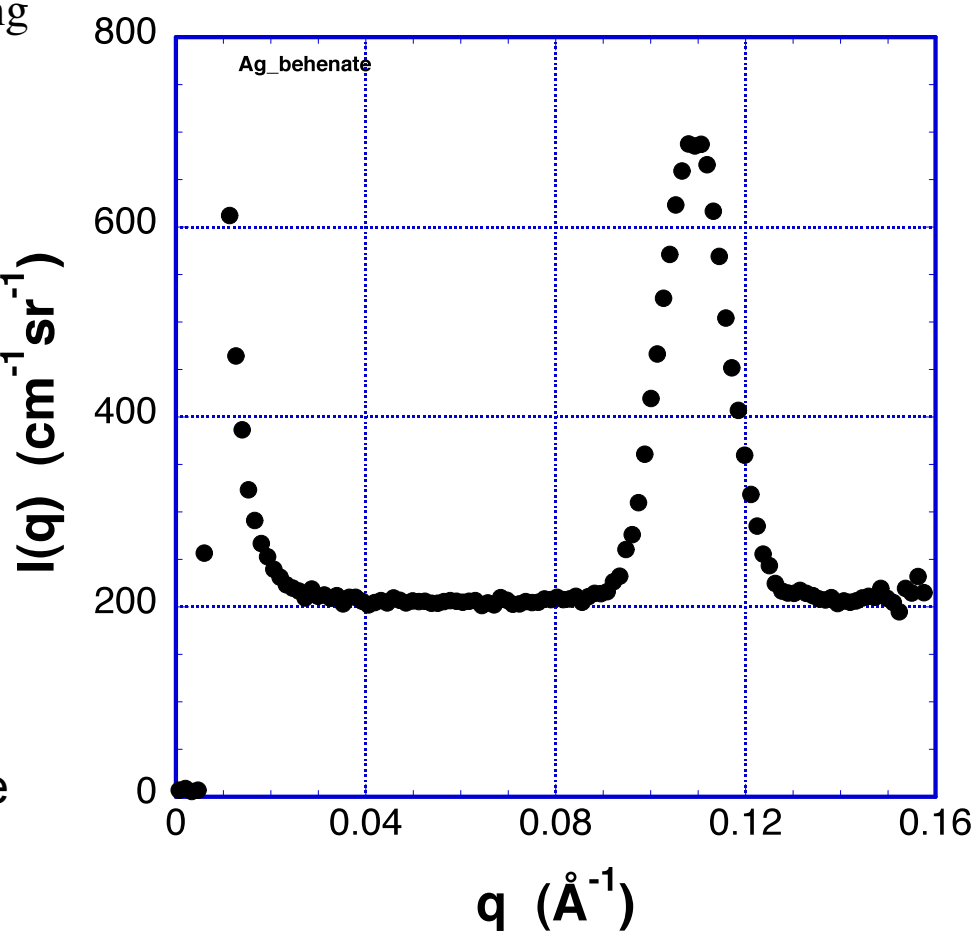
Comments

1) Works well for both Xrays and Neutrons. (Xray has better contrast)

2) q_{pk} often too large: $q_{pk} > q_{max}$

3) Accuracy unaffected by multiple scattering

SANS, peak width from instrument resolution



Scattering from **Correlation Peaks** at smaller q:

•Control pore glasses

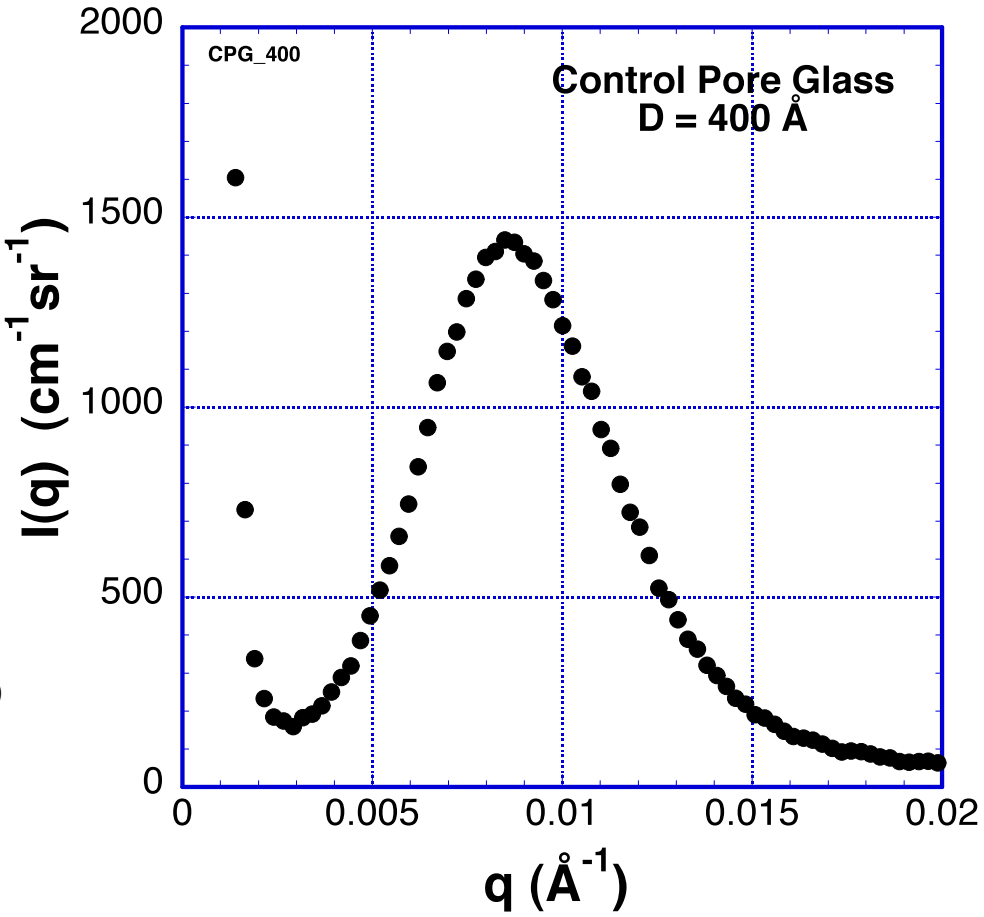
•Opal

Comments

1)Peak position must be independently calibrated

2)Strong scattering

3)Peak position is insensitive to multiple scattering



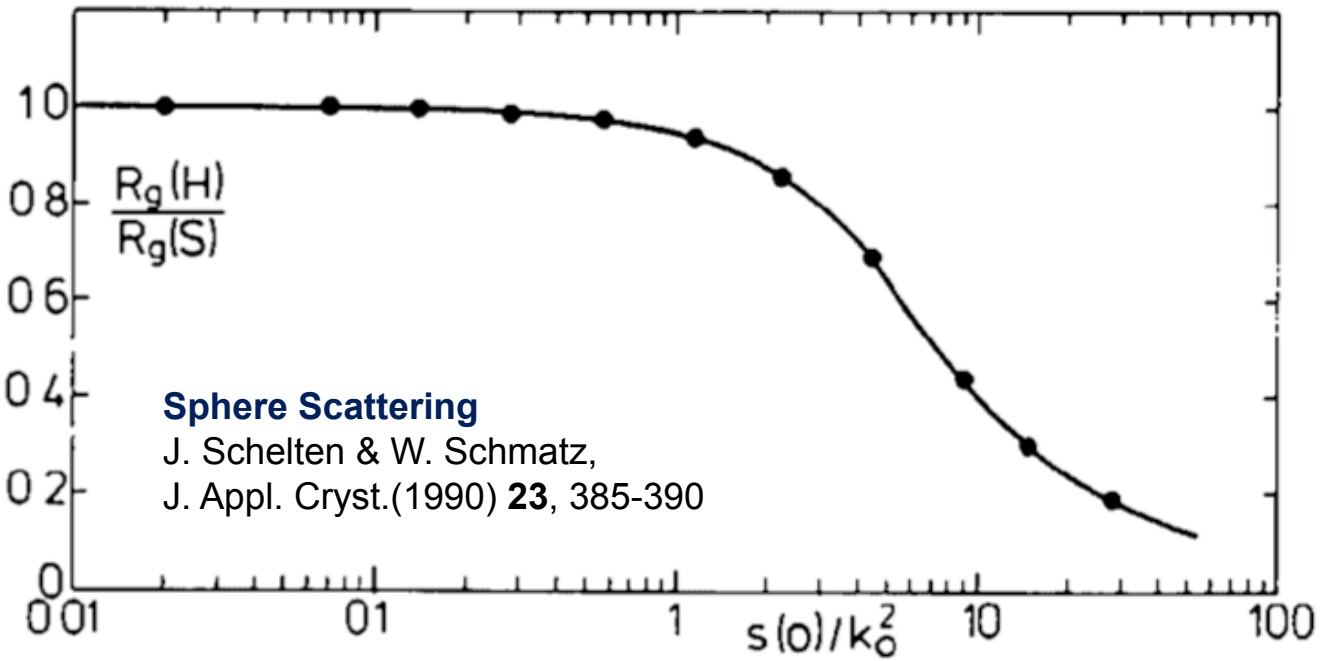
Guinier Radius fits also work well for many samples

•Primary **q**-standards (monodisperse spheres, polymer blends):

•Secondary **q**-standards (often obtained from experiments).

• Sample often used as **I(q)** standard also.

•But strong **multiple scattering** causes beam broadening lowering R_G



Wavelength Determination

• Must independently calibrate

Scattering angle θ

Xrays:

• Shell ground state (Cu-k_α)

• Absorption edge

Neutrons:

•Time-of-Flight

•Bragg scattering edge

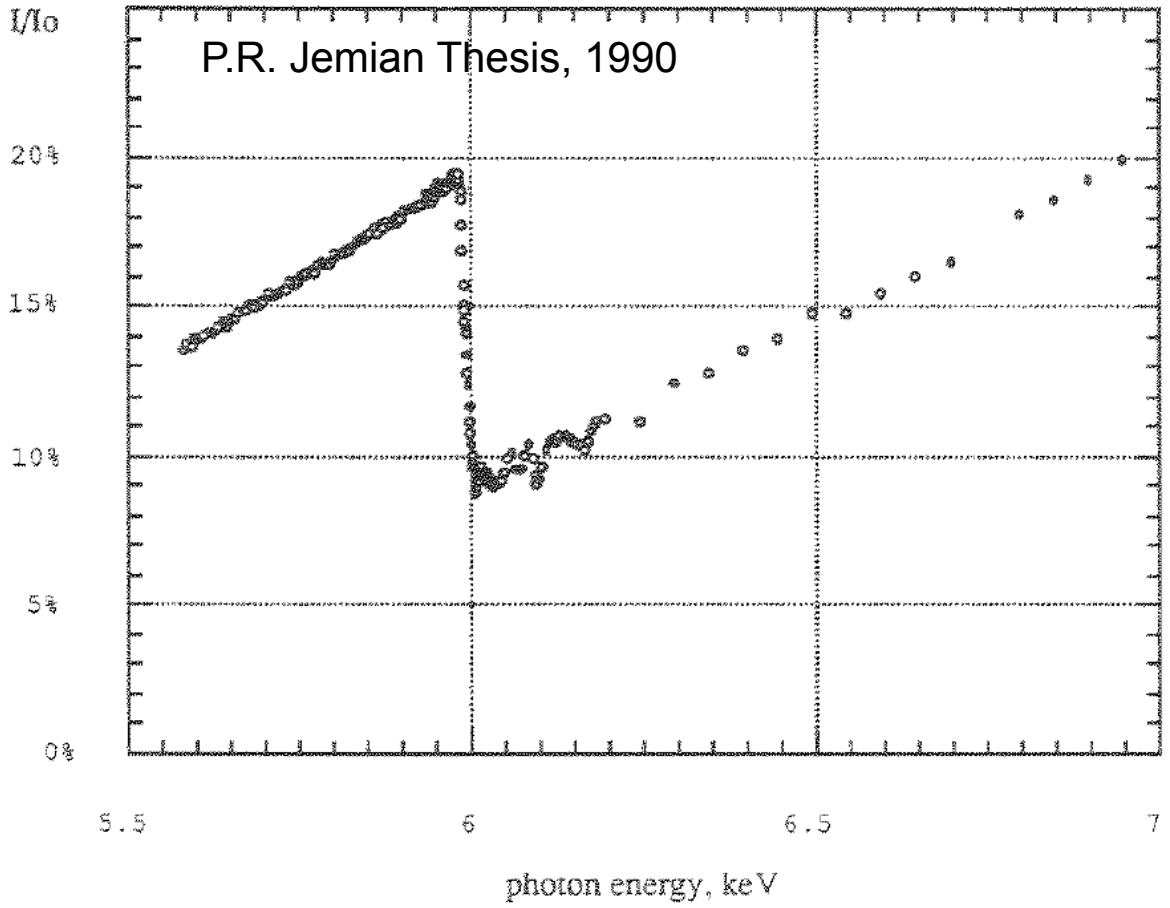
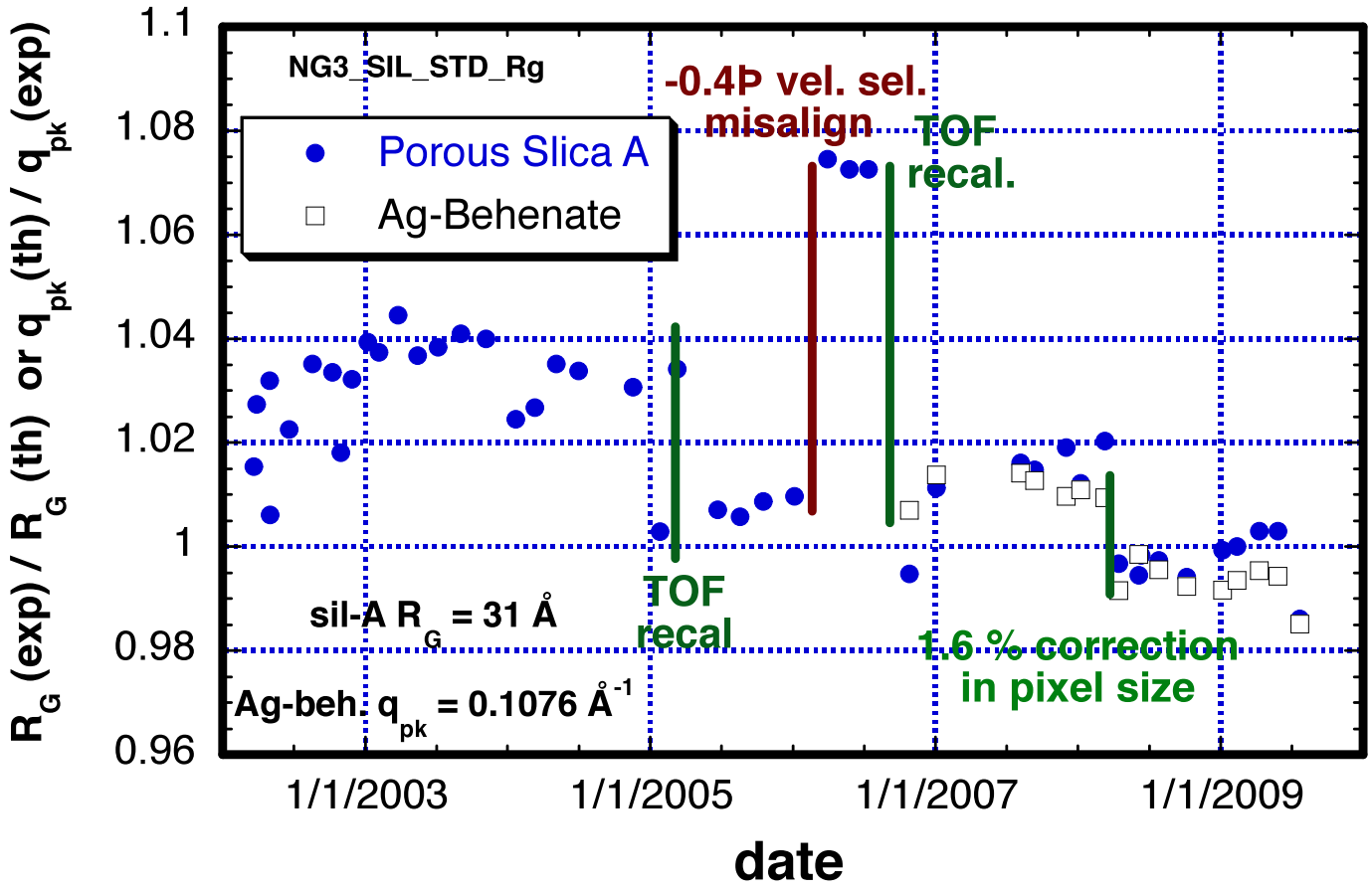


Fig. 19. *Transmission coefficient, I/I_o, of a normalized and tempered Modified Fe9Cr1Mo steel as a function of X-ray energy in the vicinity of the Cr absorption edge (5.989 keV).*

History of wavelength calibration on NG3 SANS, NCNR

- Use Guinier radius for Porous Silica std. $R_G = 31$ Å
- Use Bragg peak for Ag-Behenate $q_{pk} = 0.1076$ Å^{-1}



Absolute Intensity Calibration

$$\frac{d\Sigma}{d\Omega}(q_i) = \frac{I(q_i)}{tT\varepsilon_D I_B \Delta\Omega_i}$$

$I(q_i)$ = total counts in i^{th} annuli, normalized by monitor
I_B = counts on sample, normalized by monitor
t = sample thickness
T = sample transmission
ε_D = detector efficiency
$\Delta\Omega$ = solid angle of I^{th} annuli

1. Measure SAS from calibrated sample

- Primary std: sample scattering known independently
- Secondary std: was calibrated by primary std or by 1)

2. Measure Beam Current I_B

- Integration detector system capable of high countrate
- Calibrated beam attenuator
- Second (calibrated) low efficiency detector
- Often part of sample transmission measurement

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C.A. Dreiss, et al J. Appl. Cryst.(2006) **39**, 32-38

Water scattering from a Bench top SAXS Camera:

- Primary intensity standard
- Poor signal to noise
- Long (18 hr) counting time

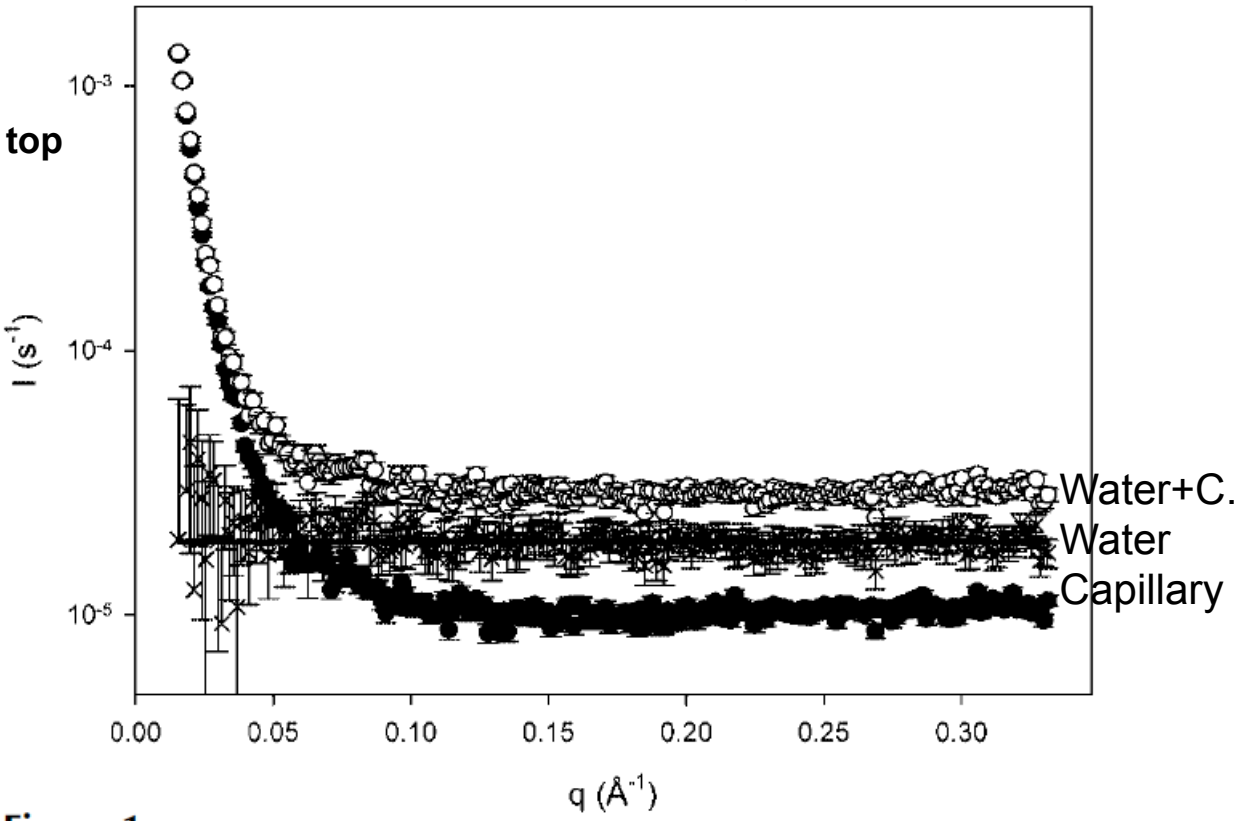
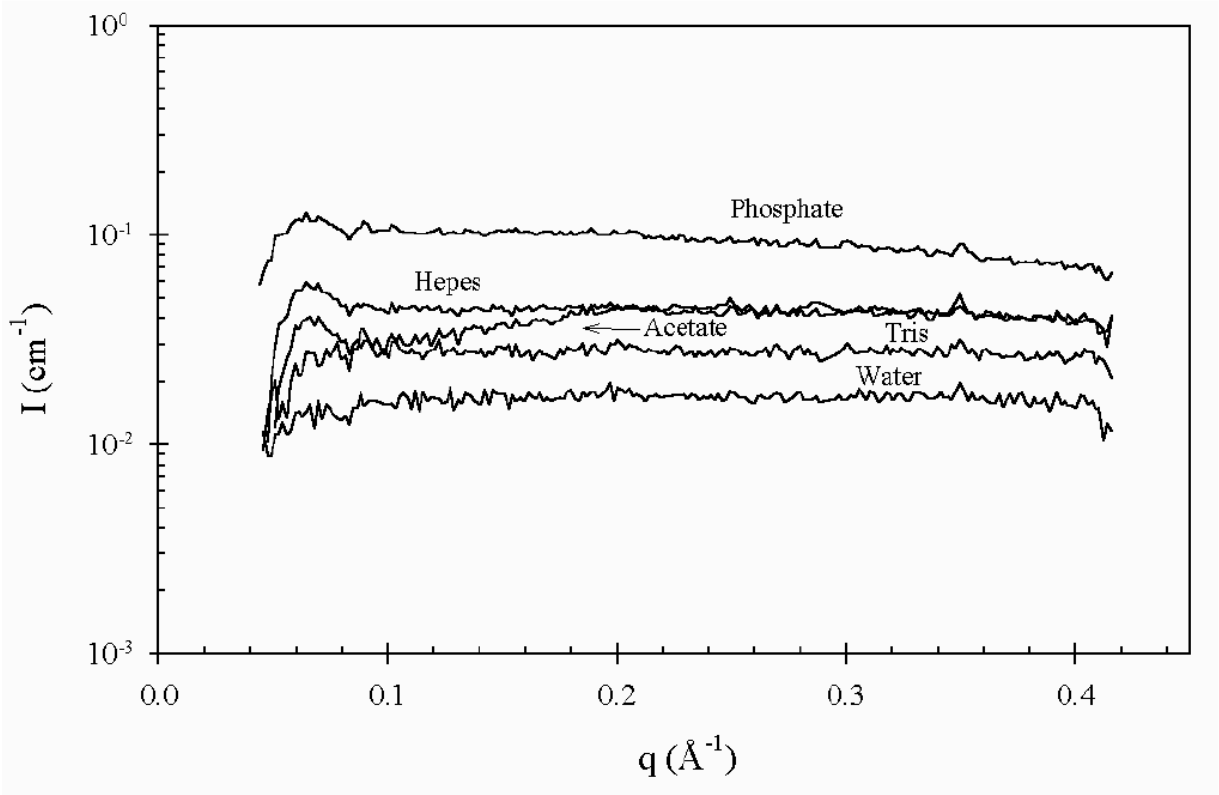


Figure 1

X-ray scattering of the empty capillary (filled circles), of the capillary filled with water (open circles), and water alone (crosses), after subtraction of the empty cell. The scattering from the empty capillary is multiplied by the transmission of water T_{H_2O}. Each sample was measured for two series of 18 h. The dark current was subtracted from all measurements. The continuous line is the fit to the flat background.

But water and other solvent/solutions are SAXS primary standards
{ Need only compressibility, density and composition }



T. Zemb, et al J. Appl. Cryst.(1990) **23**, 800-805

SANS

• **Water** commonly used

• But note difference in water scattering between D11 and D22 due to differences in Detector **efficiency.**

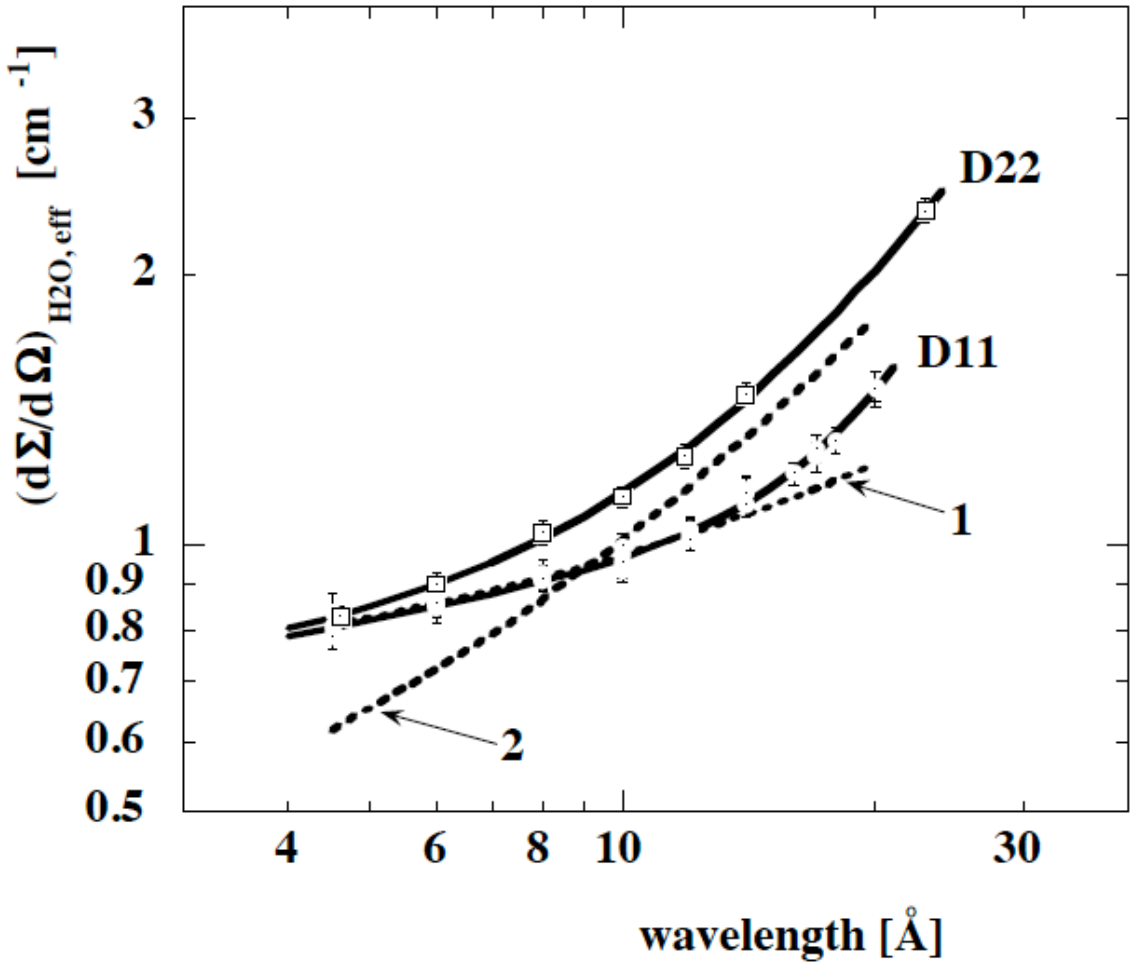
• Vanadium

• **t = 4.5 mm, 20 mm dia.**

• **T = 0.49, λ = 6 A,**

• **I(q) = 0.034 $cm^{-1}sr^{-1}$**

• **Six times weaker than water but primary std.**



P. Lindner, J. Appl. Cryst.(2000) **33,** 807-811

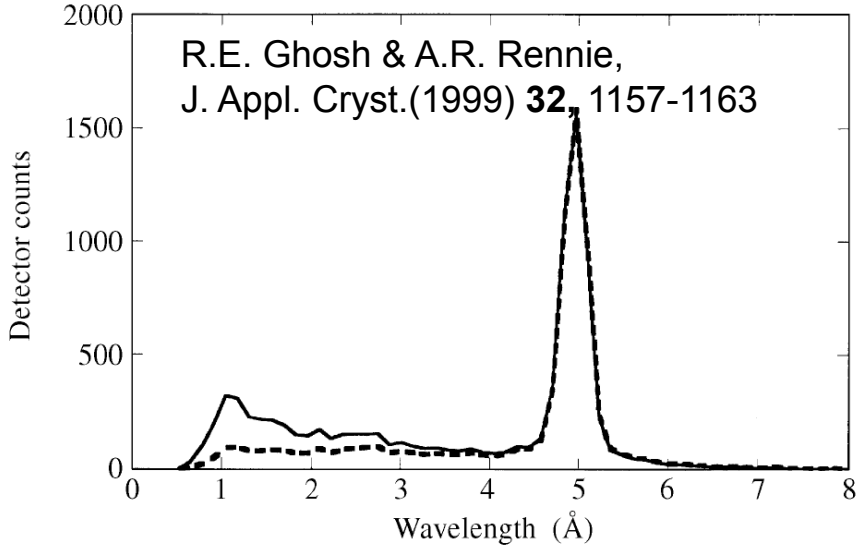


Fig. 1. Spectrum of scattered neutrons for water at $4 \pm 0.5°$, indicating the difference between data uncorrected (dashed line) and corrected (continuous line) for detector efficiency. The incident wavelength was 5 Å.

P. Lindner, J. Appl. Cryst.(2000) **33,** 807-811

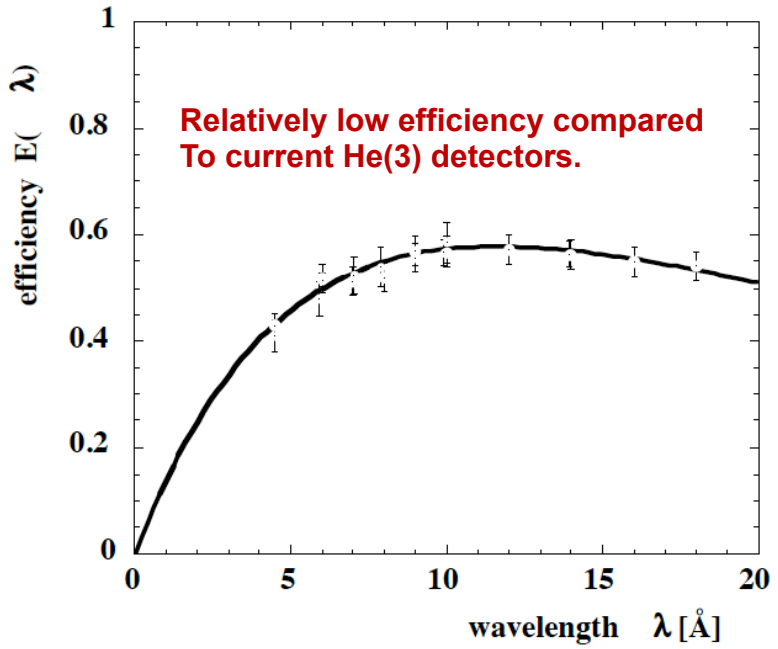


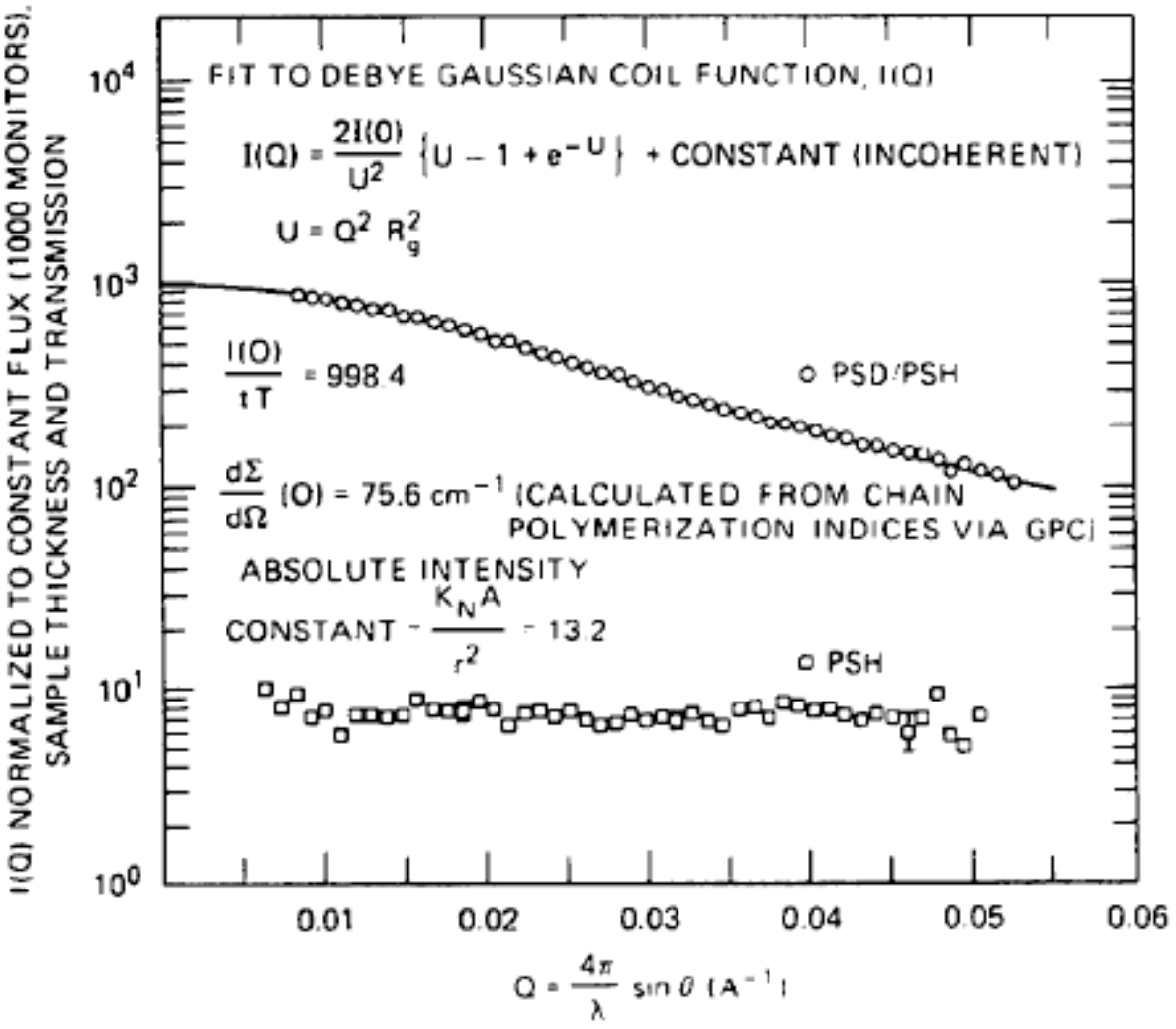
Figure 3
Efficiency $E(\lambda)$ of the D11-BF_3 detector.

- Low detector Efficiency at short (1 -2 A) wavelengths reduces I(q) measured.
- But also makes I(q) depend on **differences** between detectors (high/low efficiency)
- Need separate calibration for each detector, wavelength and sample geometry

D-H Polymer Blends

- **Primary SANS Std (RPA Equation)**
- **Limit on R_G or M_W**

G.D. Wignall & F.S. Bates, J. Appl. Cryst.(1987) **20**, 28-40



Lupolen (HDPE) is a common SAXS standard.

Note scattering from high density Polyethylene depends upon Sample characteristics.

T.P. Russell, et al J. Appl. Cryst.(1988) **21**, 629-638

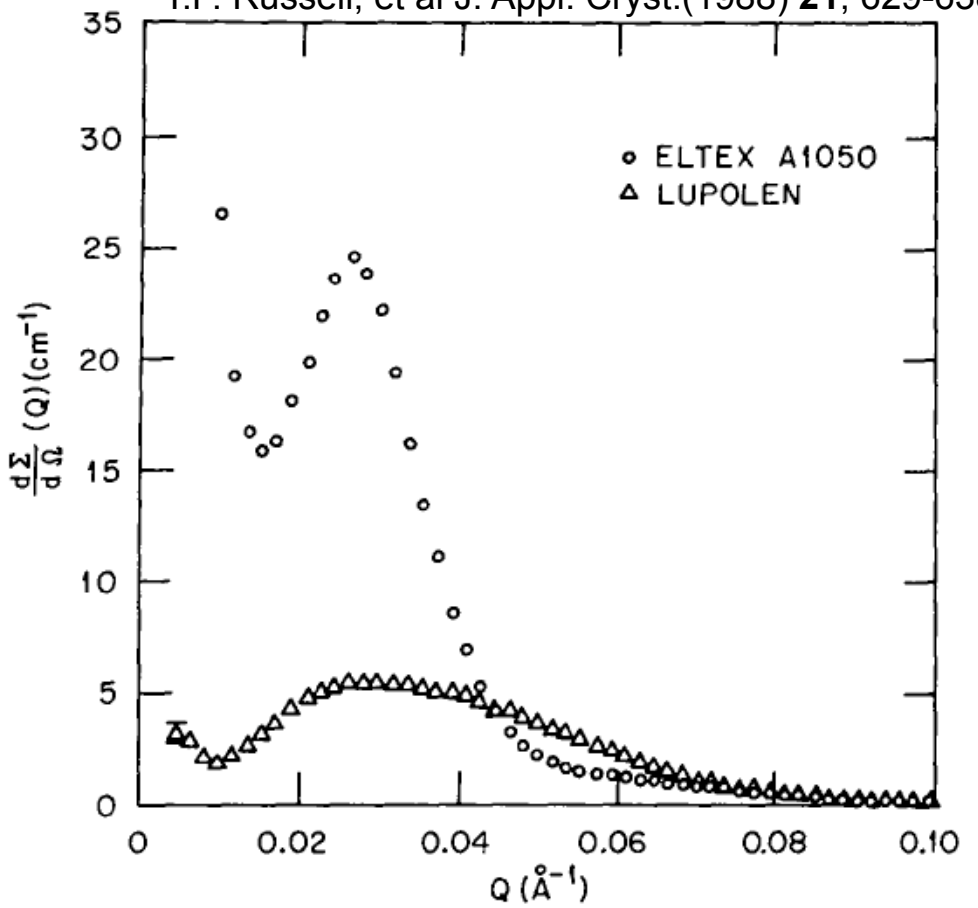


Fig. 4. $d\Sigma(Q)/d\Omega$ *versus* Q for Eltex A1050 and Lupolen (Kratky) standards (ORNL 10 m SANS).

Colloids made from monodisperse SIO_2 particles are excellent Standards if made with long term **Stability**….

C.A. Dreiss, et al J. Appl. Cryst.(2006) **39**, 32-38

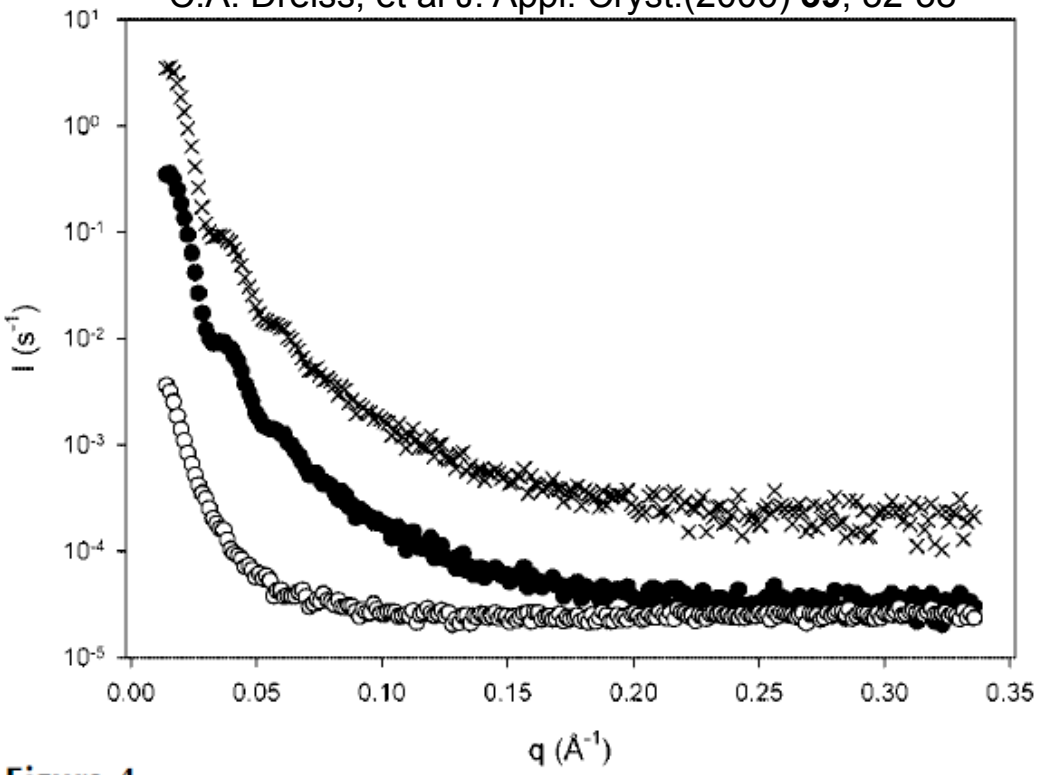


Figure 4
X-ray scattering of a 3% (*w*/*w*) suspension of silica contained in a quartz capillary (filled circles), of the empty capillary (open circles), and of the suspension of silica after subtraction of the empty cell (crosses) (scaled by a factor of 10, for clarity). The silica suspension was measured for 1 h, the empty capillary for 18 h and the dark current was subtracted from all samples. The error bars are smaller than the symbols and are not shown here.

Colloid particles can be

Stabilized within **elastomer**

Matrix.

Difficult to make???

T.P. Russell, et al J. Appl. Cryst.(1988) **21**, 629-638

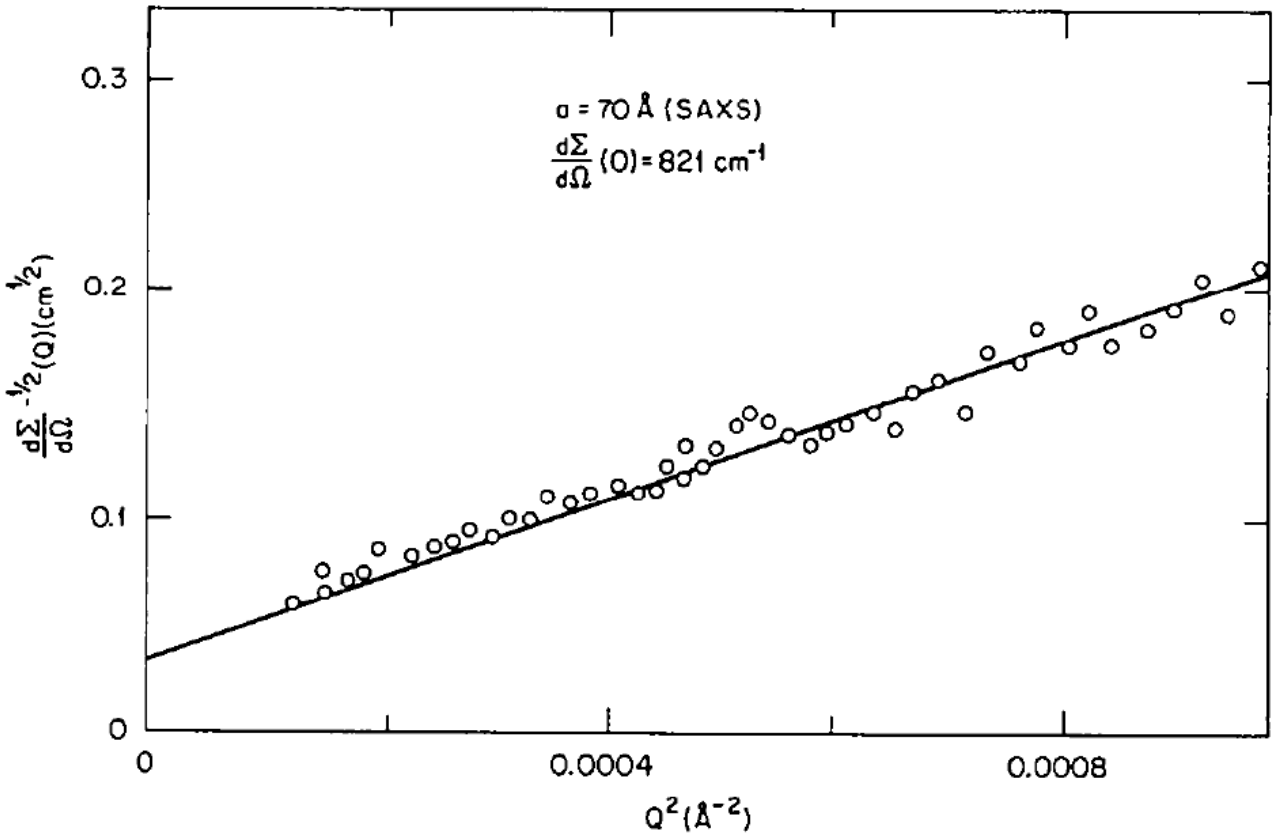
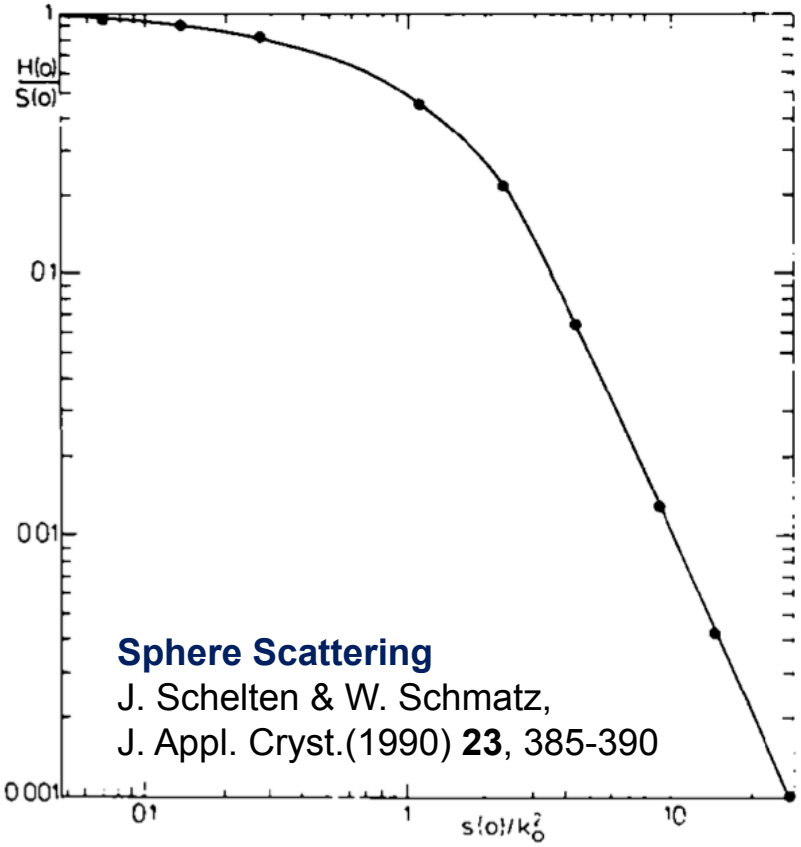


Fig. 8. Debye–Bueche plot for 5·0 wt% SiO_2 in polyisobutylene (SAXS).

Effect of Multiple Scattering on the Absolute Intensity Scale

- Curve can be shifted **up or down** depending T measurement
- **Shape** of scattering also matters….



Sphere Scattering
J. Schelten & W. Schmatz,
J. Appl. Cryst.(1990) **23**, 385-390

$$\tau = -\ln(T_{SAS})$$

P. Strunz, et al J. Appl. Cryst.(2000) **33**, 829-833

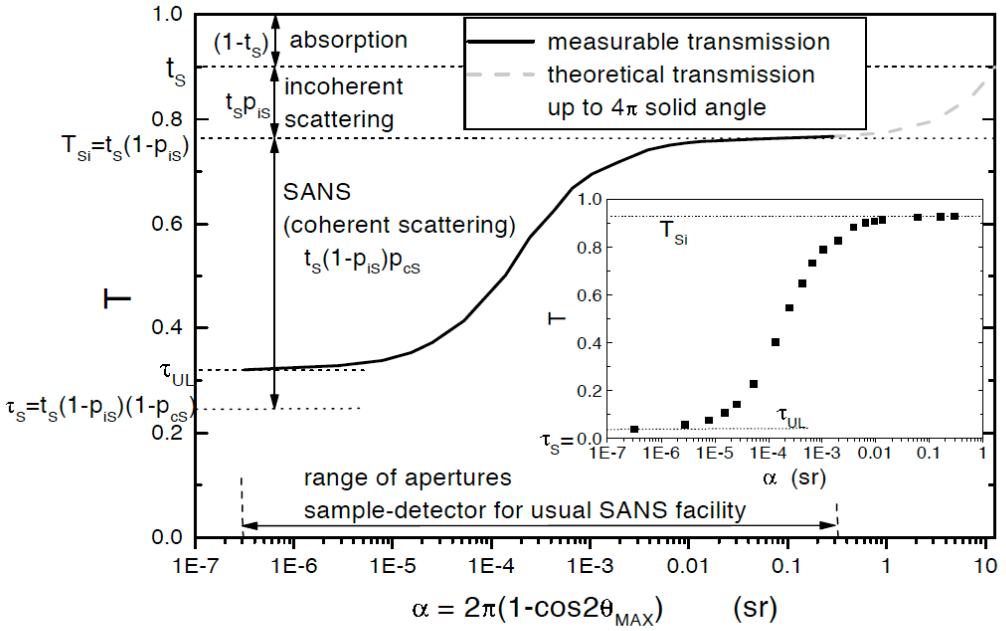
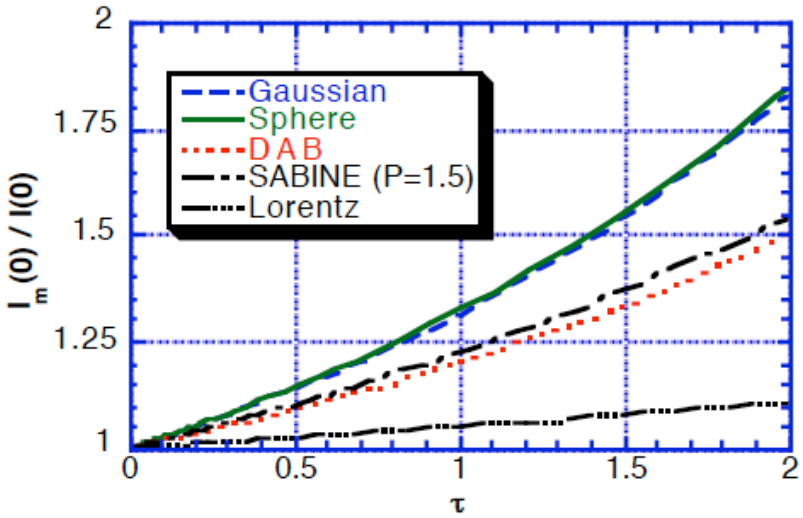
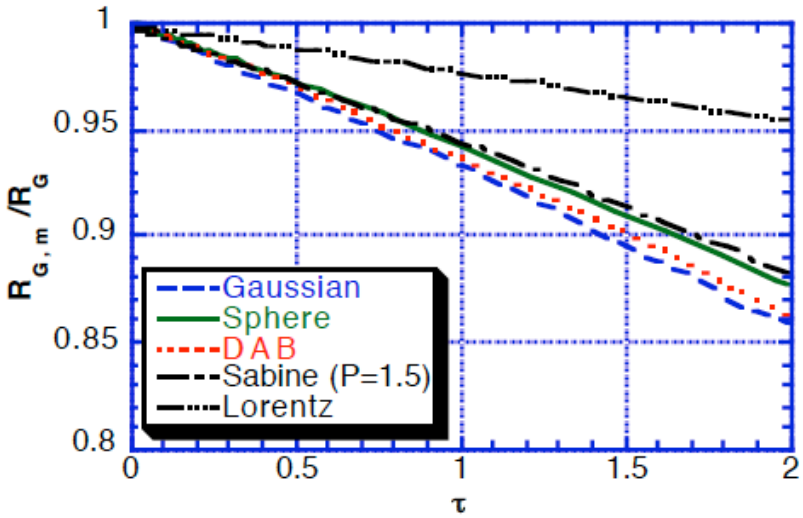


Figure 1
The basic scheme of the transmission measurement. Inset: measured transmission for a porous plasma-sprayed alumina layer.

Dependence of multiple scattering correction to R_G and I(0) for

Different **shapes** of scattering functions:



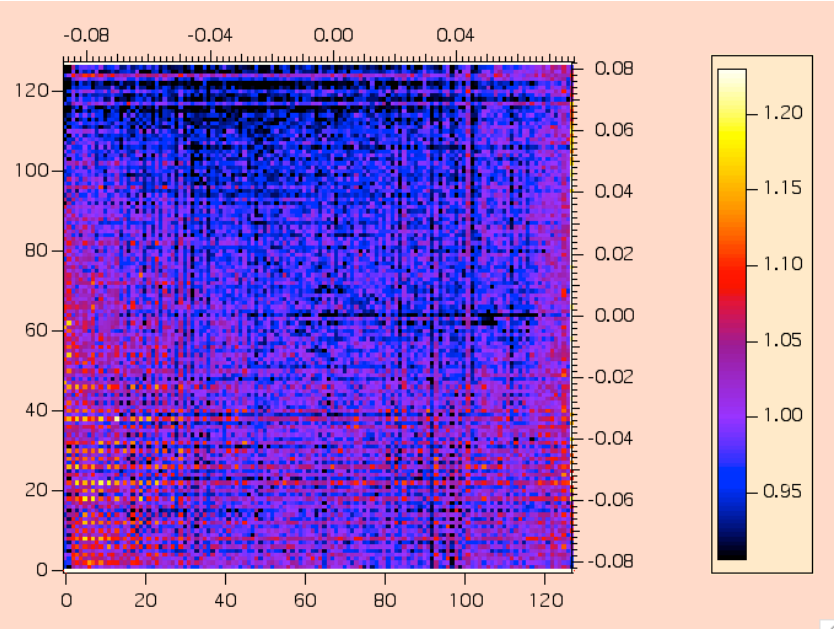


What appears to be minor damage to anode wire from sensitivity image (left) causes large

Error in beam current determination for small beam at higher pixel count rate.

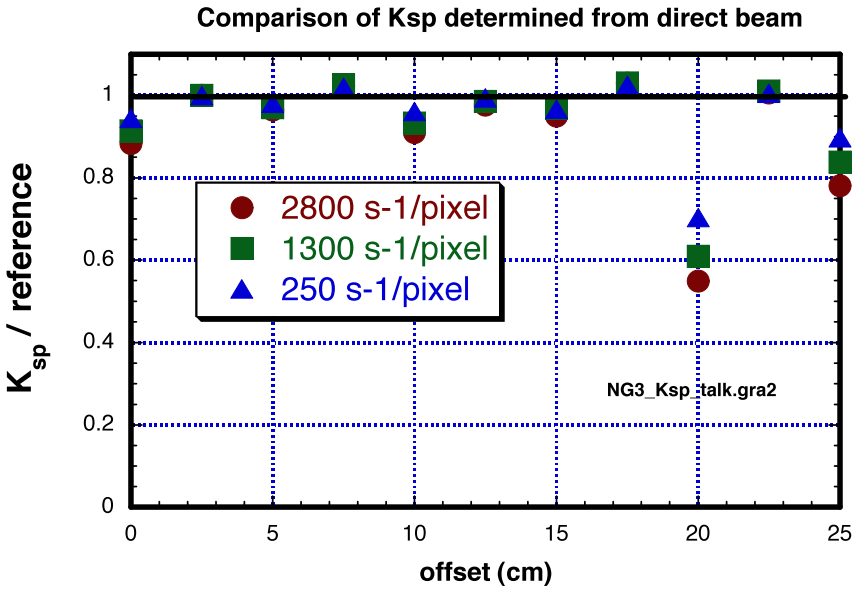
Plexiglass sensitivity 2 s^{-1} / pixel

Minor reduction in efficiency **~ -5 %**



High count rate in 4 pixel (small) beam

Major reduction: **-40 %**



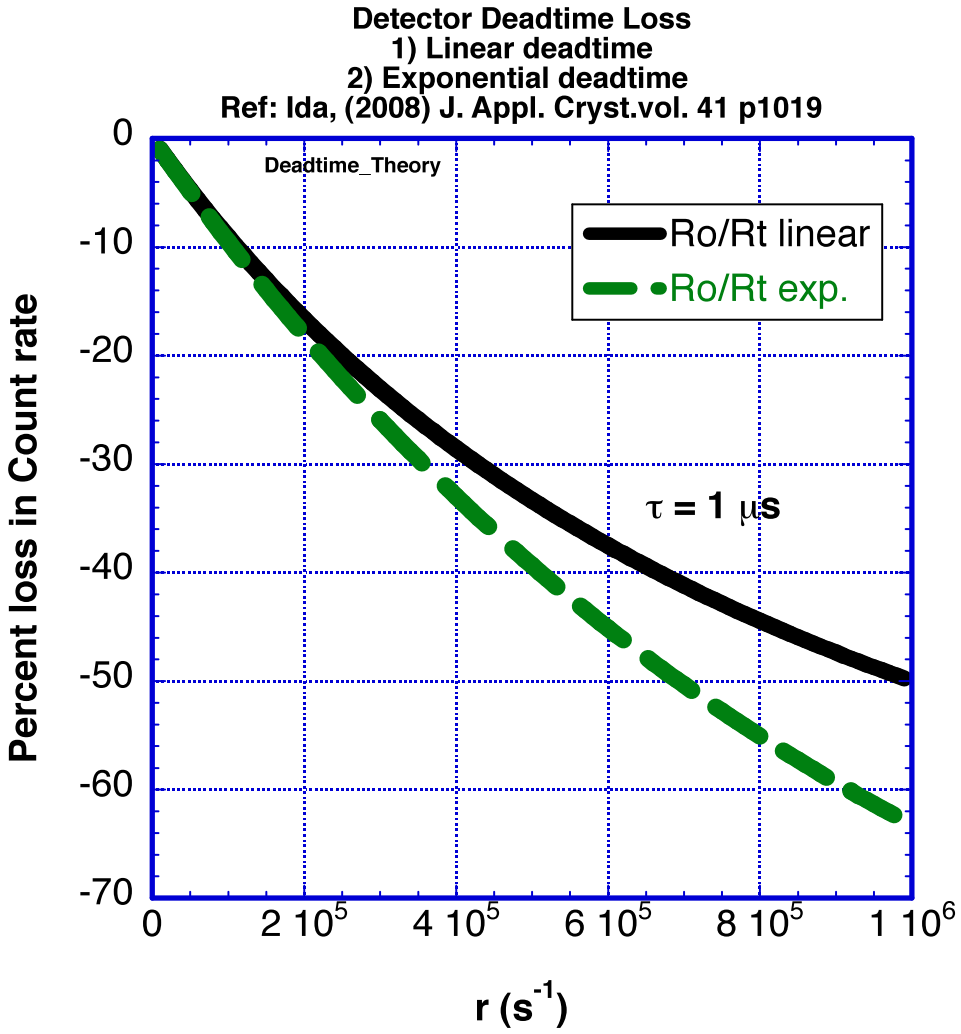
Detector Dead time Corrections

(For counting detectors…)

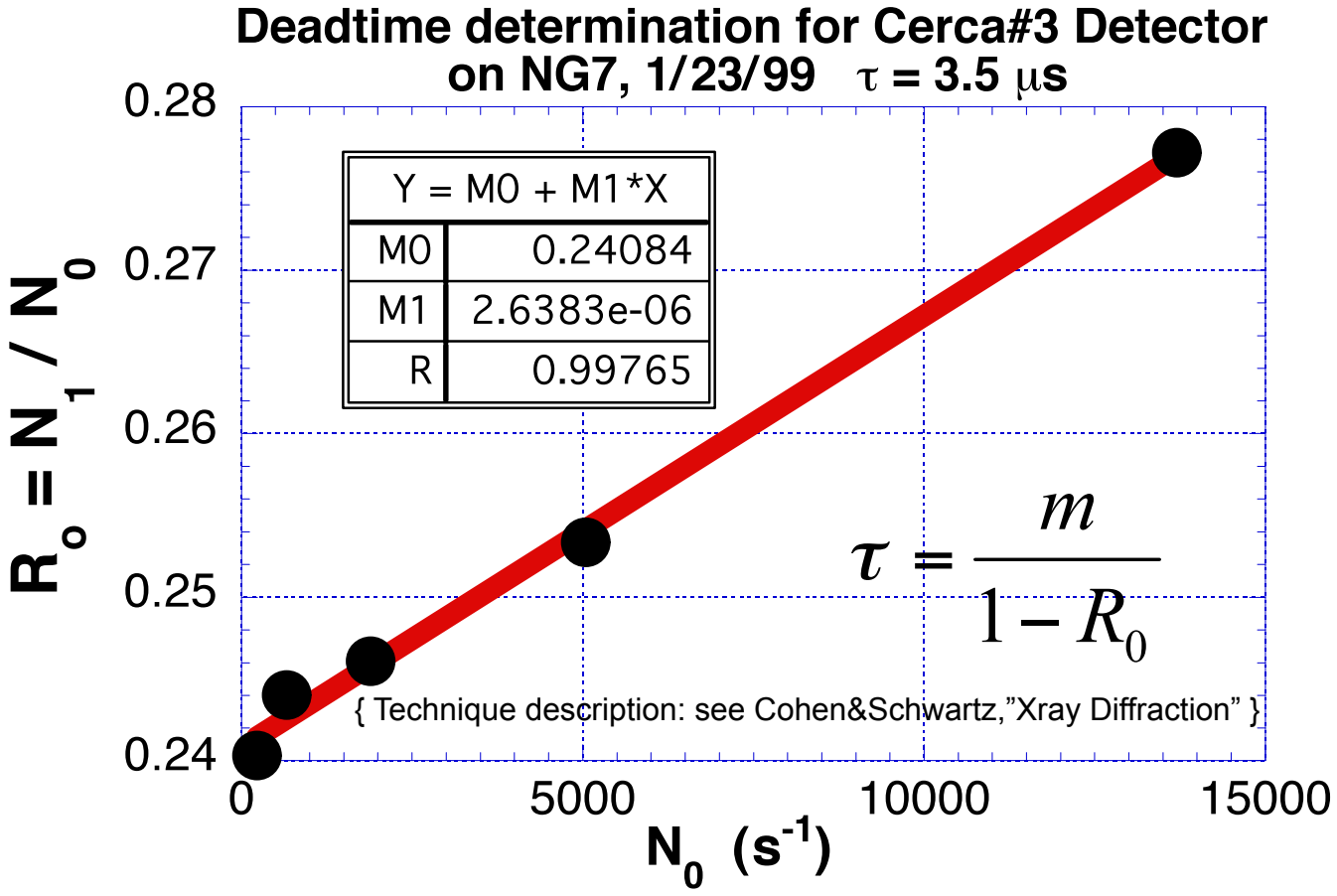
Two models of correction based

Upon electronics:

- **Linear**
- **Exponential**



At NIST, we measure the detector count rate of large direct beam with two different Size apertures (6 mm and 12 mm) and than vary count rate with large aperture By inserting plastic (PMMA) beam attenuators.



Summary

Q-scale standards

• Ag-Behenate is good q-standard for both SAXS and SANS if q_{pk} is within q-range.

• Many other I-standards also work as q-standards (via R_G).

• Must be vigilant in Q&A testing at reactor SANS facilities due to common yaw rotation misalignment of velocity selector.

I-scale standards

1.Qualities of a good standard

- Sample scatters strongly within current instrument configuration q-range.
- But not so strongly as to cause significant multiple scattering or detector dead time.
- **STABLE** to one percent in I(q) over decades.
- Readily available and inexpensive.

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Primary Standards: samples that can have I(q) calculated independently from scattering measurements .

Xrays: Liquid (water, pentane, etc) scattering originating from compressibility.

• Scattering too weak for general use. Can be used to calibrate secondary standards or check direct beam methods.

Neutrons:

• **Deuterated+Hydrogenated linear polymer blends**

  • Cross-section known from M_W (from GPC), % deuteration and chi parameter.

  • Scattering can be tailored to q-range via M_W for R_G

  • Scattering strength controlled by % deuteration and volume fraction.

• **Vanadium single Crystal**

  • Can calculate I(q) using Monte Carlo simulation of sample and beam dimensions and neutron wavelength for absorption.

  • Single crystals are expensive and limited in size.

  • Sample can absorb hydrogen altering I(q).

Xrays: Intensity Standards:

Sample	Pros	Cons
Glassy carbon	Strong scatterer	Hard to adjust strength
Polyethylene (Lupolen)	Moderate scatterer	Hard to adjust strength
Particles (SiO_2) in Elastomer	Stable, adjustable	Difficult manufacture
Water, pentane	Primary std, available	Weak scatter
Multiple experimenter's samples	Calibrated & available	Custom manufacture limits obtaining more sample

Neutrons Intensity Standards:

Sample	Pros	Cons
Water	Strong scatterer, available	Calibrate for cell dimensions, wavelength & detector
D-H Polymer blends	Primary std, adjustable	Expensive, difficult to obtain
Colloid solutions (polystyrene)	Scattering strength adjustable	Unstable from sedimentation
Particles (SiO_2) in Elastomer	Stable, adjustable	Difficult manufacture
Vanadium	Primary std, moderate scatterer	Simulate multiple scattering correction
Multiple experimenter's samples	Calibrated & available	Custom manufacture limits obtaining more sample

Neutron wavelength sensitive to Velocity Selector "yaw" rotation alignment.

{ Rotation speed accurate to 0.1 % }

Transmission of Copper (Barker, thesis)

$T = \exp(-\mu t)$

$\mu_{th} = \mu_{inc} + A\lambda = (0.0466 + 0.1779*\lambda)\ cm^{-1}$

< Five different Facilities >

Two recalibrations after inadvertent yaw Rotation of velocity selector.

~20 samples per visit but often

Could not compare results between visits…

Quick test with λ-standard sample would have resolved concern…

Particle size $V_P \propto (\phi/S_V)^3 \propto q^{-12}$