X-ray Radiometry

Small Angle X-ray Scattering for the Determination of Nanoparticle Concentration

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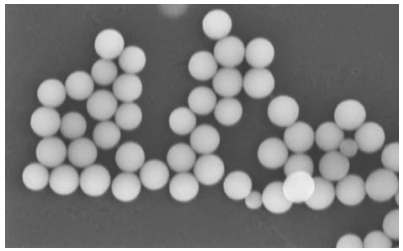
IAWG and SAWG Joint Workshop
Techniques used in CCQM-P194 to determine the gold nanoparticle number concentration

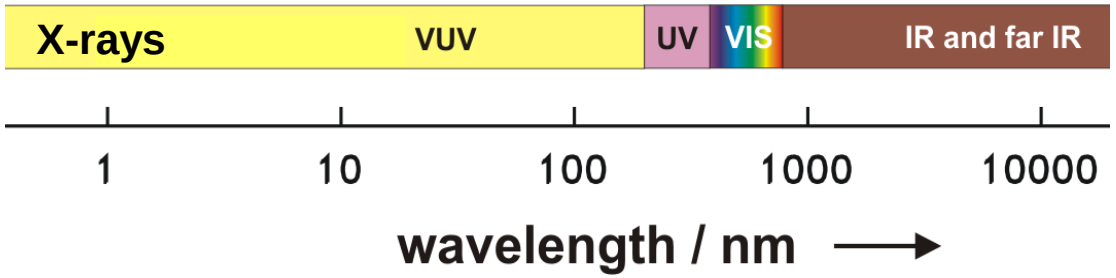
BIPM, Sèvres
8th April 2019

Small Angle X-ray Scattering (SAXS)

X-ray Radiometry

Why X-rays?





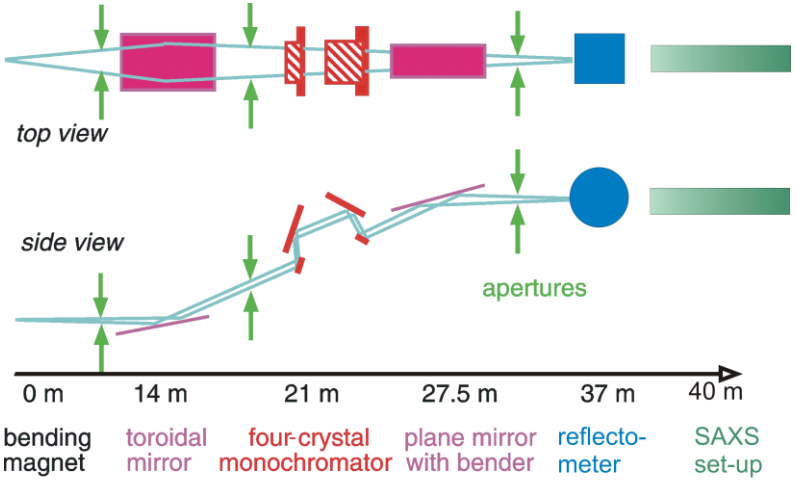
- Wavelength of the radiation < 0.5 nm, well suited to study particles in the diameter range from a few nm up to several hundred nm
- SAXS is an ensemble technique (like DLS)
- Particles can be investigated in suspension
- Scattering sensitive to electron density contrast
- Straightforward scattering theory (form factor), traceability!

PTB approach: primary method

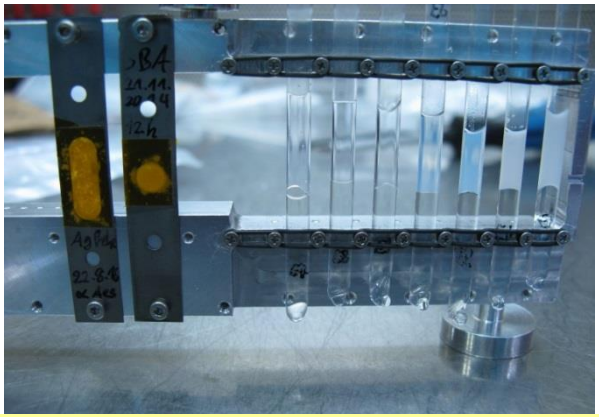
X-ray Radiometry

Synchrotron radiation facility BESSY II

FCM beamline



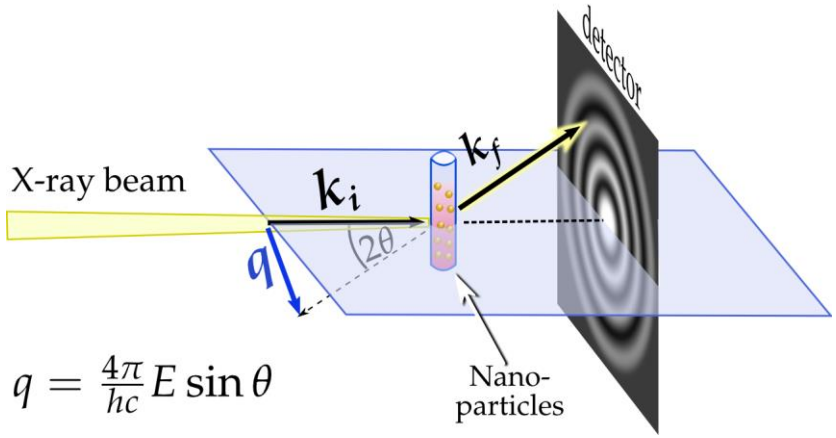
- dedicated in vacuum SAXS detector
- sample – detector distance up to 4.5 m

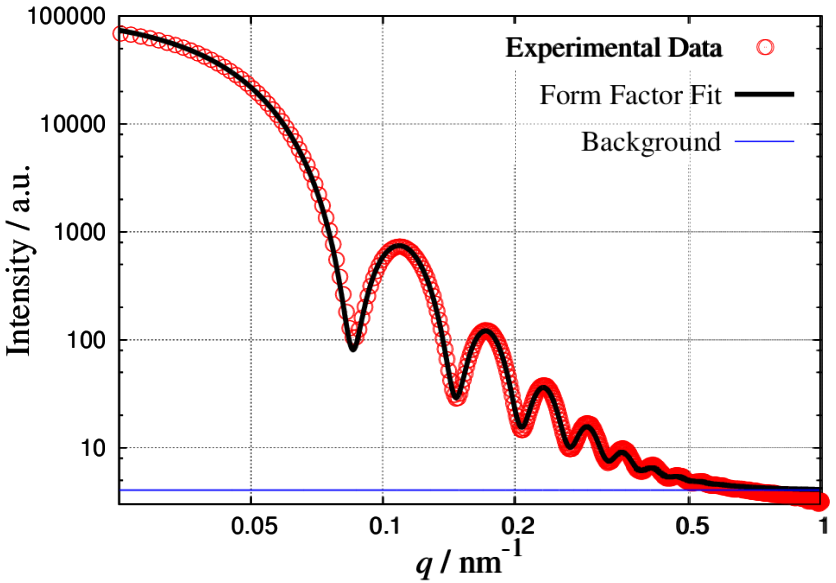


J. Wernecke, C. Gollwitzer, P. Müller and M. Krumrey, J. Synchrotron Rad. 21, 529 (2014)

Traceable SAXS

X-ray Radiometry





Model fitting for sufficiently monodisperse particles:

- period of oscillations can be connected to the X-ray wavelength
- size can be made traceable to the SI unit meter

For size measurements, only the *q*-axis needs to be traceable

For concentration measurements, also the 'intensity' needs to be traceable

PTB approach: primary method

X-ray Radiometry

Direct measurement of all relevant parameters

For the *q*-axis, required for size determination:

- Photon energy *E*
- Distance between sample and detector *L*
- Detector pixel size *s*
- (Model fitting)

$$I \approx \langle f^2(q,R) \rangle$$

$$f(q,R) = \frac{4}{3}\pi R^3 \left(3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3} \right)$$

For the scattered intensity, additionally required for concentration:

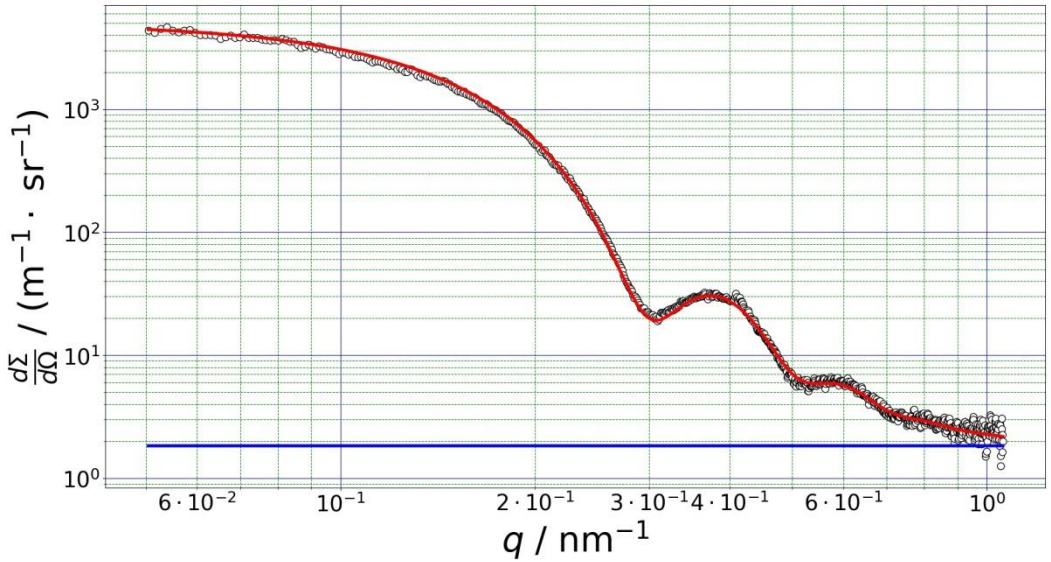
- Differentially scattered photon flux $d\Sigma/d\Omega$
- Incident photon flux Φ_0
- Detection efficiency η_{QE}
- Sample transmittance *T*
- Sample thickness *w*
- Electron density difference $\Delta\rho_e$

$$\frac{d\Sigma}{d\Omega}(q) = r_e^2 \cdot C \cdot \Delta\rho_e^2 \int_0^\infty g(R) \cdot |f(q,R)|^2 dR$$

$$\frac{d\Sigma}{d\Omega}(q) = \frac{I_{meas}(q)}{\Phi_0 \cdot T \cdot \Delta\Omega \cdot t_{exp} \cdot \eta_{QE} \cdot w}$$

Number concentration determination

X-ray Radiometry



Au NP, CCQM 0650

Nominal diameter 30 nm
Measured diameter 29.1 nm

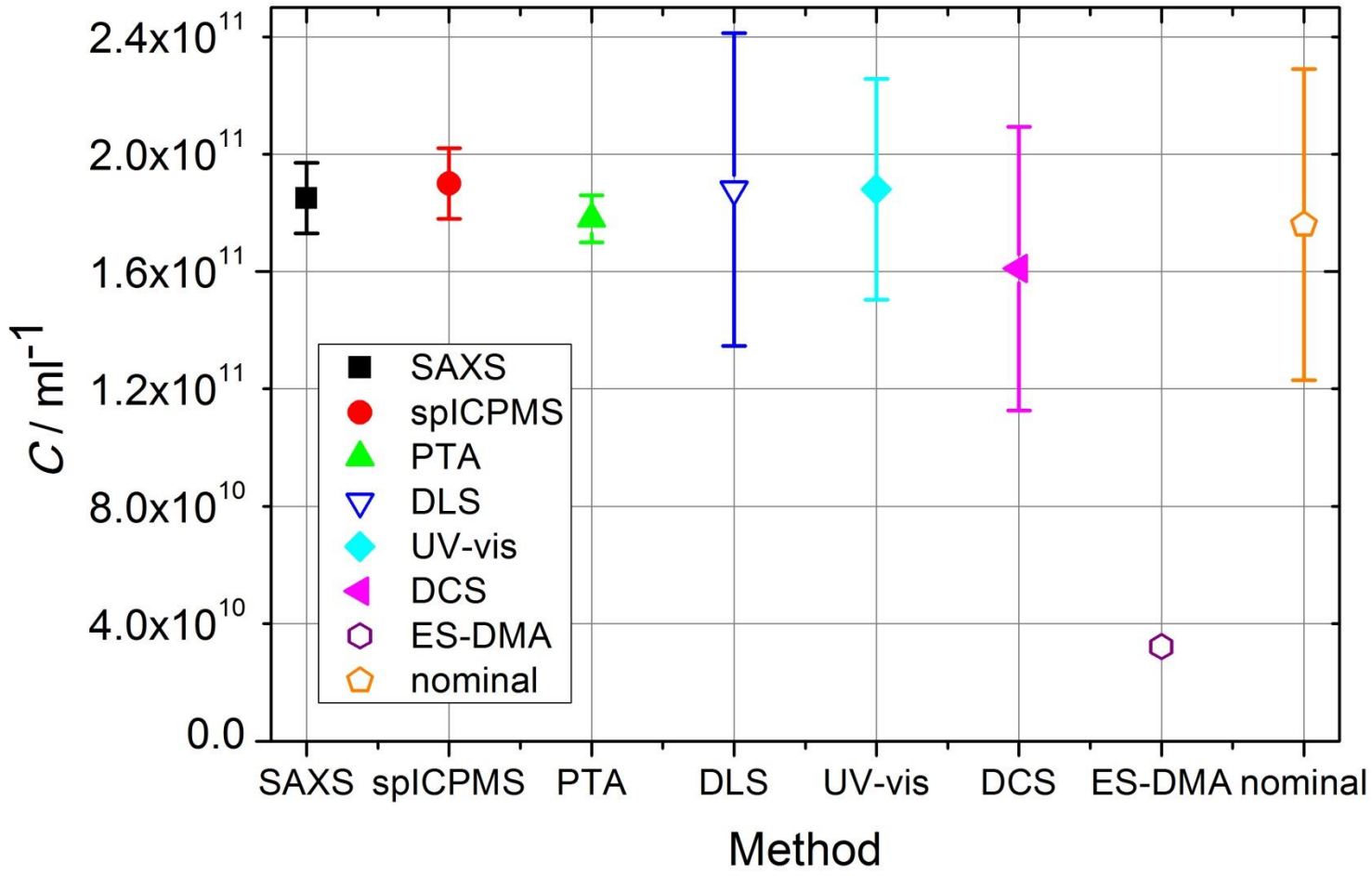
Uncertainty budget

Input x_i	x_i · unit	$U(x_i)$ · unit	U_C/ml^{-1}
s	172.1 μm	0.2 μm	$4.6 \cdot 10^9$
L	4501 mm	5 mm	$4.4 \cdot 10^9$
Φ_0	$3.42 \cdot 10^9$ ph/s	$3.42 \cdot 10^7$ ph/s	$1.70 \cdot 10^9$
T	1.68 %	0.01 %	$1.70 \cdot 10^9$
E	8000.0 eV	0.8 eV	$4.0 \cdot 10^8$
t	150.00 s	$<$ 0.15 s	$1.70 \cdot 10^8$
η_{QE}	97 %	3 %	$6.0 \cdot 10^7$
$Nfit$	$2.49 \cdot 10^{-5}$	$1.43 \cdot 10^{-6}$	$9.8 \cdot 10^9$
w	0.981 mm	0.009 mm	$2.32 \cdot 10^9$
$(\Delta\rho)^2$	$1.88 \cdot 10^7$ nm^{-6}	$4.05 \cdot 10^4$ nm^{-6}	$3.93 \cdot 10^8$
C	$1.70 \cdot 10^{11}$ ml^{-1}		$0.10 \cdot 10^{11}$

Number concentration determination

X-ray Radiometry

EMPIR project InNanoPart, Au NP, nominal diameter 30 nm

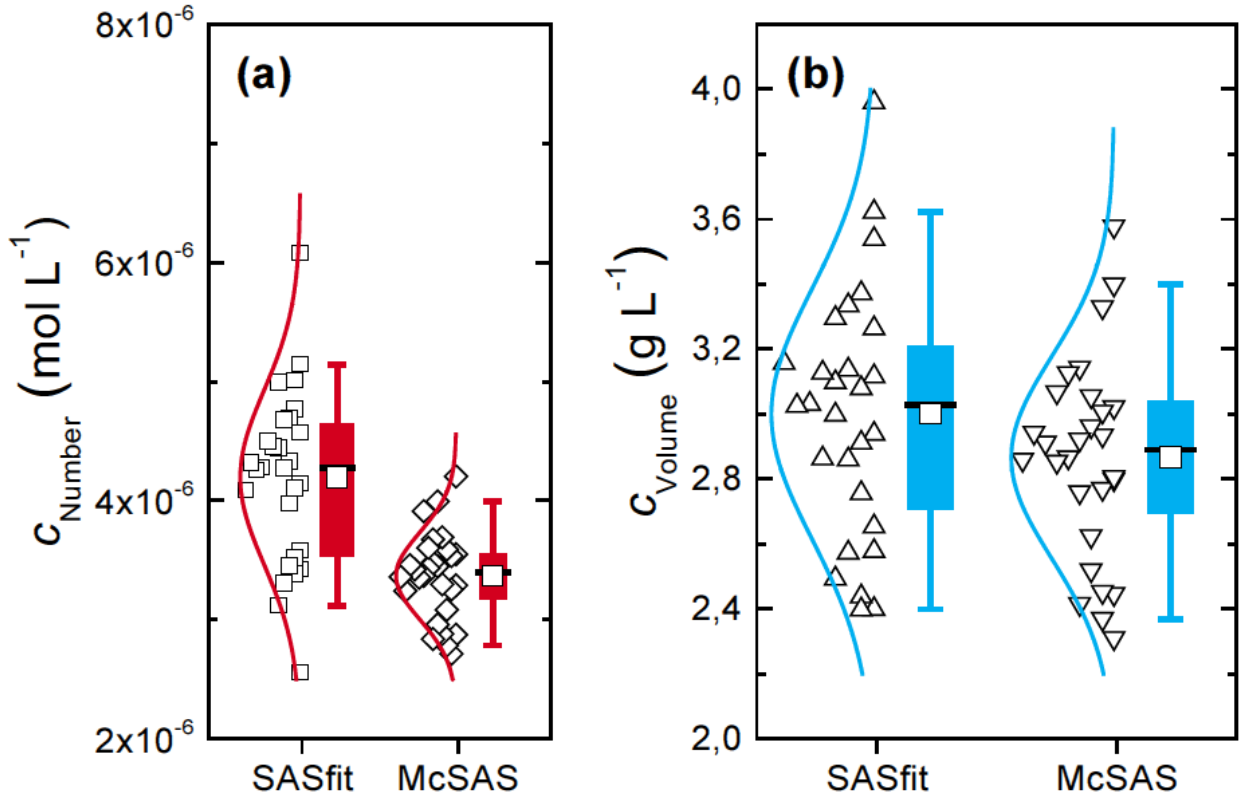


A. Schavkan *et al.* , Nanomaterials **9**, 502 (2019)

Laboratory approach: round robin

X-ray Radiometry

Recent round robin organized by BAM proves good reproducibility:
Ag particles, **diameter 6 nm**, Ag literature density



B. Pauw *et al*., J. Appl. Cryst. 50, 1280 (2017)

Conclusion

X-ray Radiometry

- Traceable size determination of spherical nanoparticles using Small-Angle X-ray Scattering (SAXS) has already been established, ISO standard 17867:2015 available
- Nanoparticle concentration determination with low uncertainties requires the knowledge or determination of all relevant parameters, including the (electron) density of the nanoparticles
- In the EMPIR project InNanoPart, SAXS and spICPMS were used as traceable reference methods for nanoparticle concentration determination
- Development of an ISO standard for nanoparticle concentration determination with SAXS has been started (ISO/PWI 23484)

Laboratory approach

X-ray Radiometry

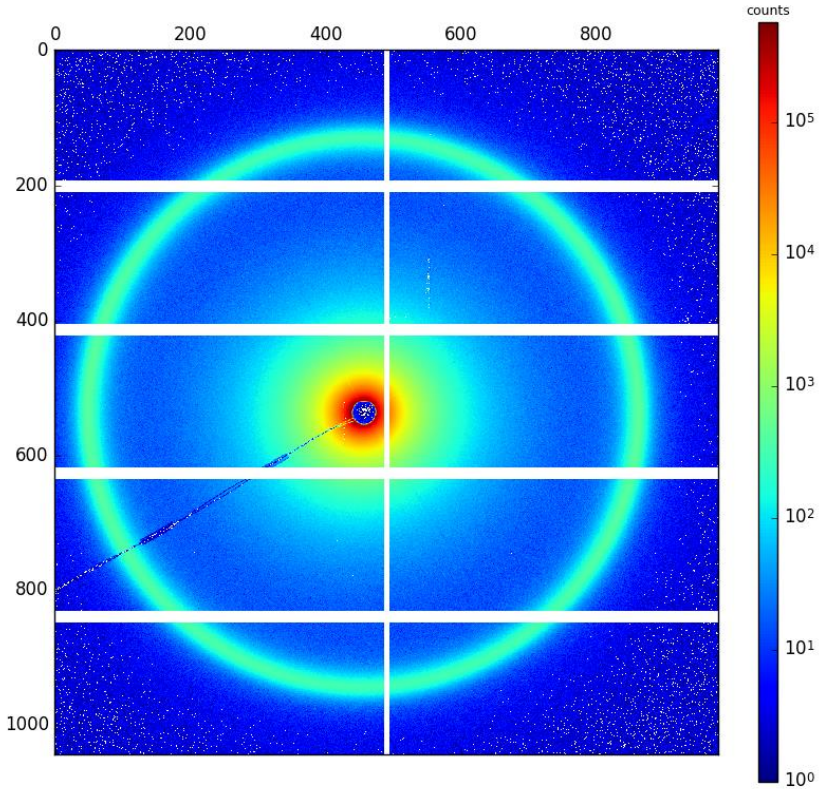
Examples for commercial SAXS Instruments

From manufacturers websites

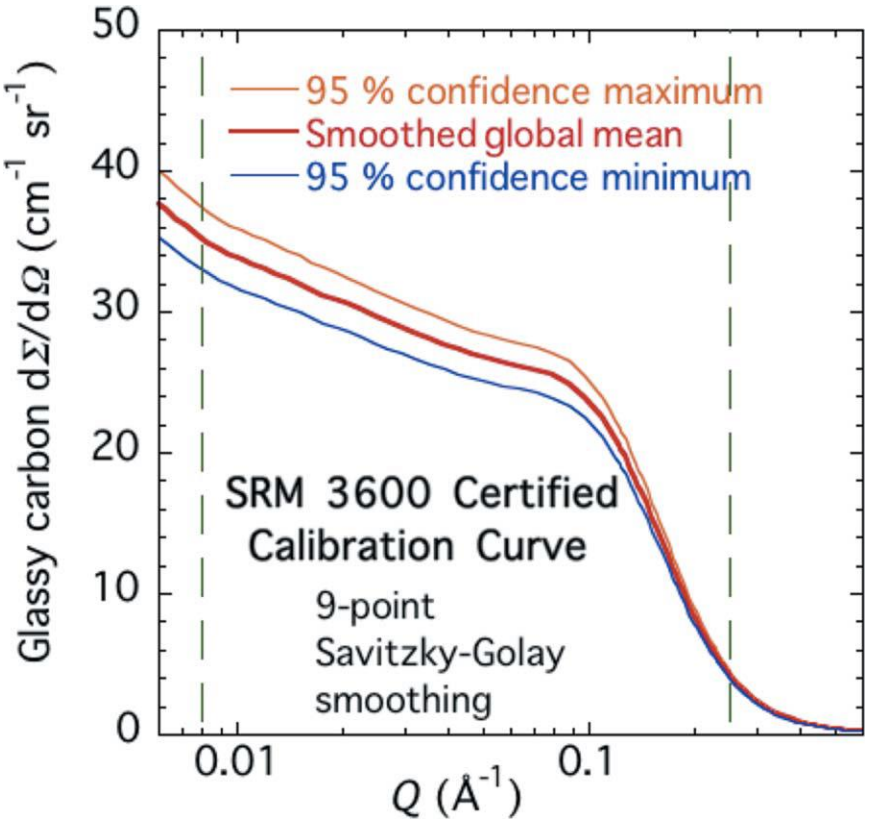
Laboratory approach

X-ray Radiometry

Reference material for *q*-axis calibration:
e. g. silver behenate



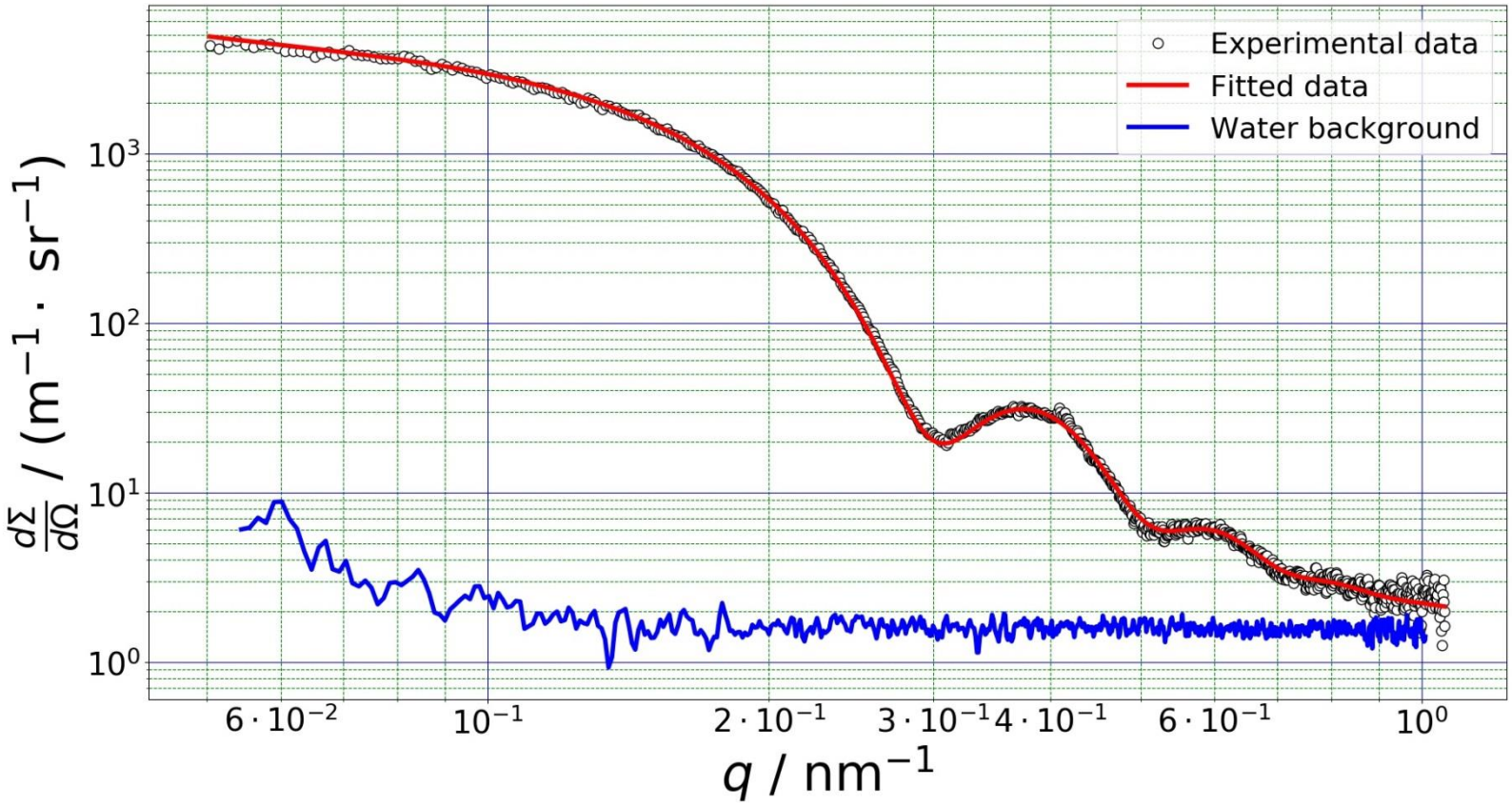
Reference material for intensity calibration: lupolen, water or glassy carbon, NIST SRM 3600



A. Allen *et al*., J. Appl. Cryst. **50**, 462 (2017)

No sorry, I don’t know the price of a commercial SAXS set-up.

Please contact the manufacturers.


Experimental data
Fitted data
Water background
$\frac{d\Sigma}{d\Omega}$ / (m^{-1} · sr^{-1})
10^3
10^2
10^1
10^0
$6 \cdot 10^{-2}$
10^{-1}
$2 \cdot 10^{-1}$
$3 \cdot 10^{-1}$
$4 \cdot 10^{-1}$
$6 \cdot 10^{-1}$
10^0
q / nm^{-1}