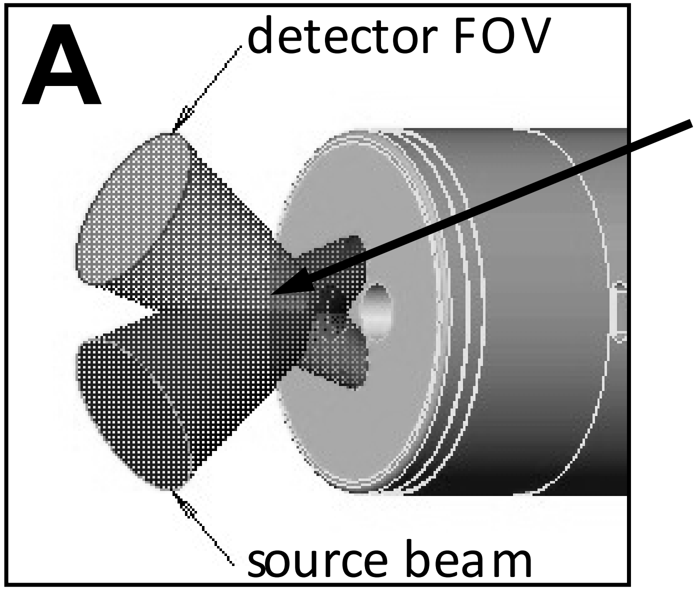
Protocols for large angle scattering measurements including polarization

Mike Twardowski

ECO type VSF measurement

β(θ) measurements are always resolved over a range of angles



Overlapping volume defines W(θ)

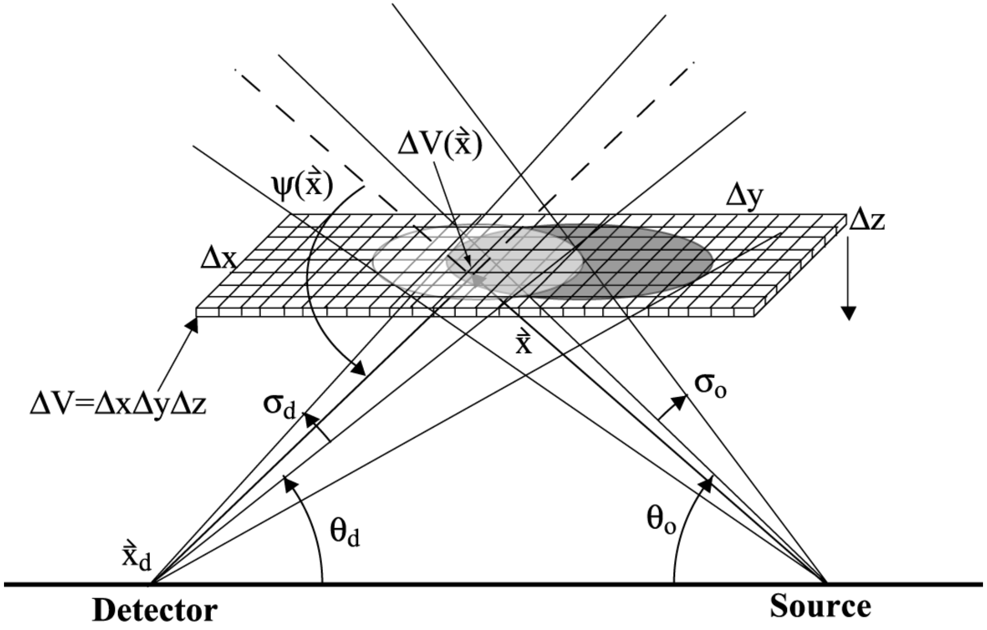
W(θ) weighting function

$\bar{\theta}$ centroid angle

$$\bar{\beta}(\bar{\theta}, \Delta\theta) = \int_0^{\pi} \beta(\theta) W(\theta)\, d\theta \qquad \bar{\theta} = \int_0^{\pi} \theta W(\theta)\, d\theta \Big/ \int_0^{\pi} W(\theta)\, d\theta$$

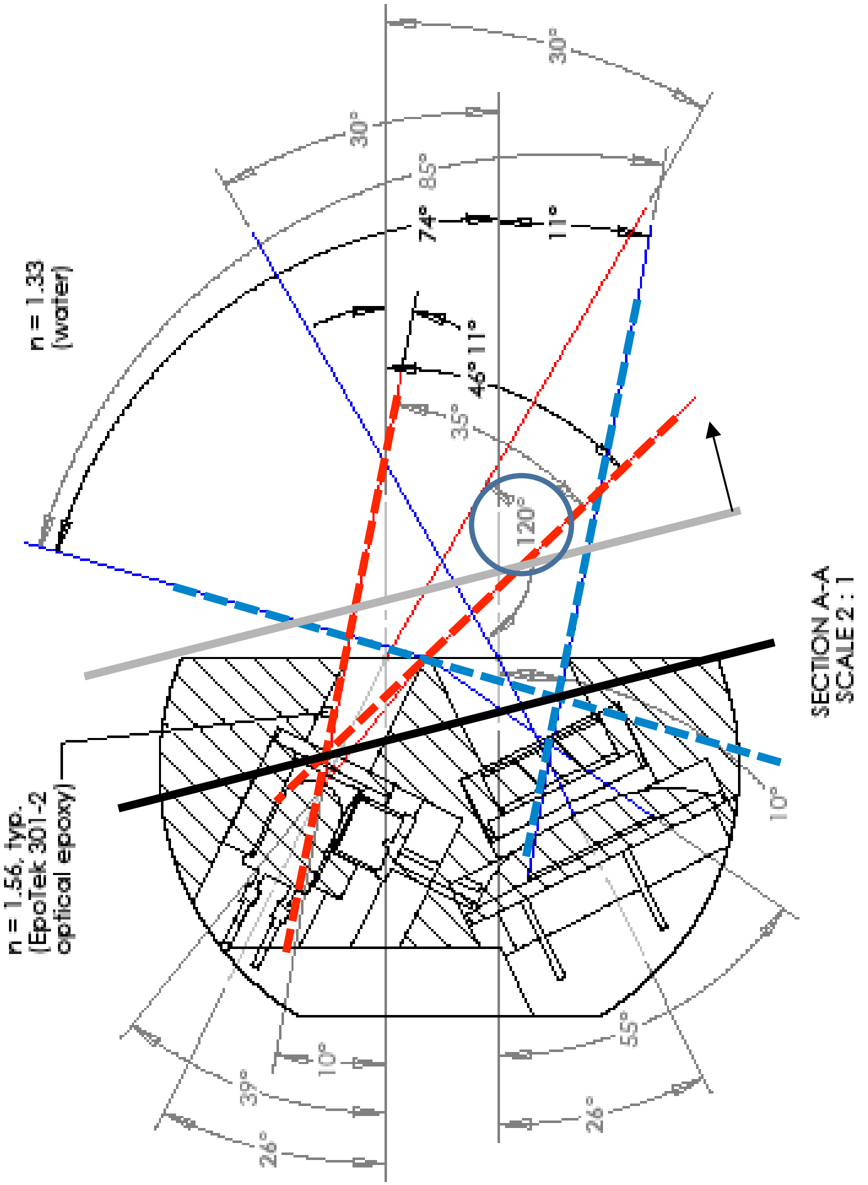
Determining W(θ)

<u>Analytically</u> (see Sullivan et al. 2013) – the “virtual plaque” method

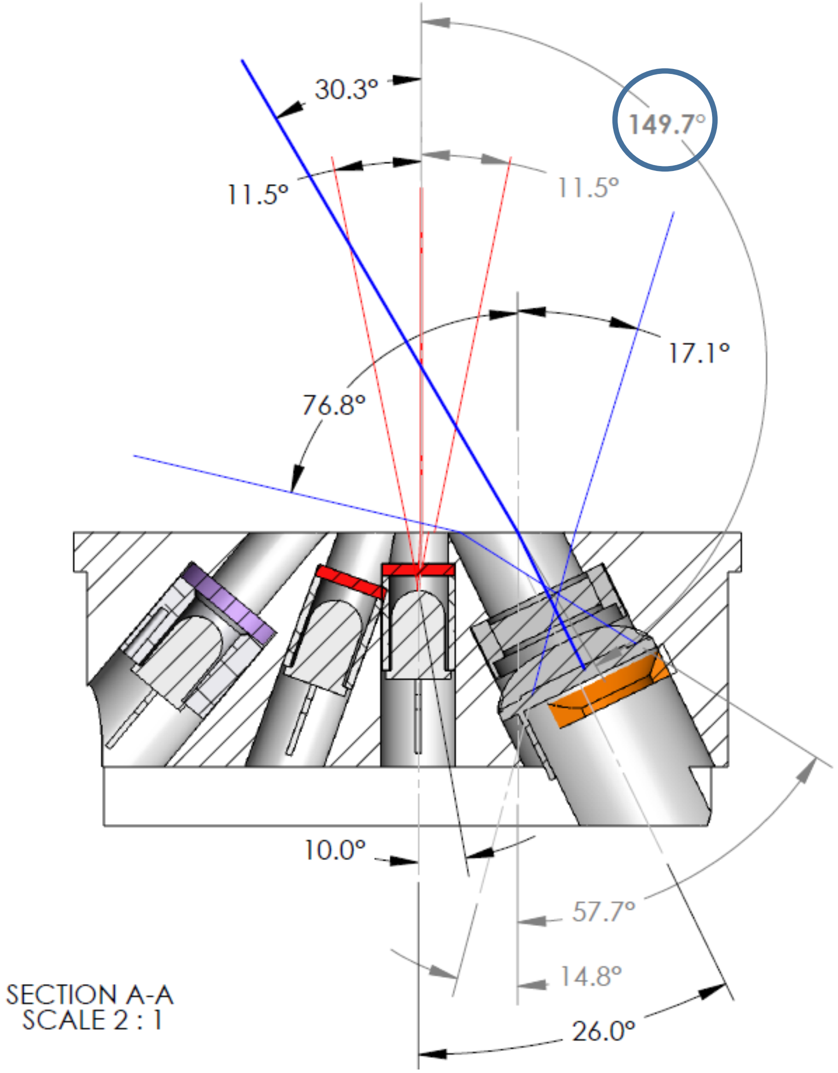


- Step virtual plaque through sample volume
- Determine area where source and detector beam images overlap for each z step
- Calculate power returned to detector at each dV in the overlapping area (note there is no consideration of VSF in doing this)
- Assign θ to each dV
- Compile results (i.e., fill θ bins) to derive weighting function

Example of actual ECO geometries

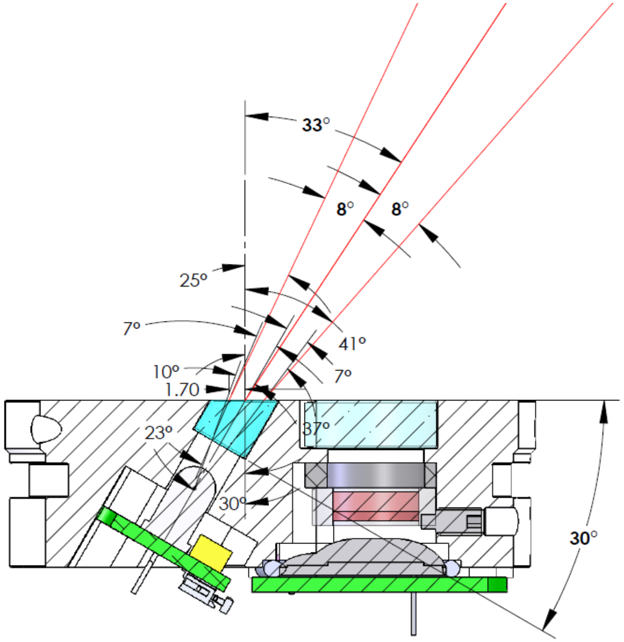


ECO-BB geometry



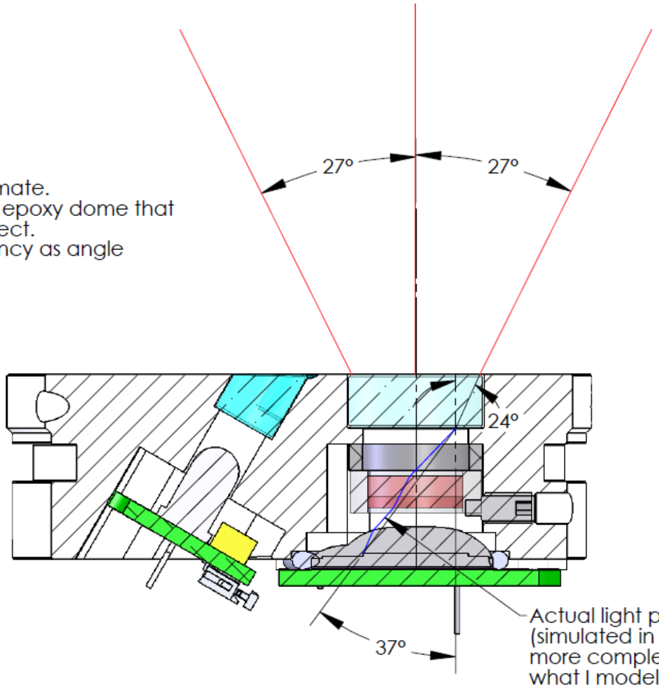
ECO-VSF geometry (150°)

MCOMS



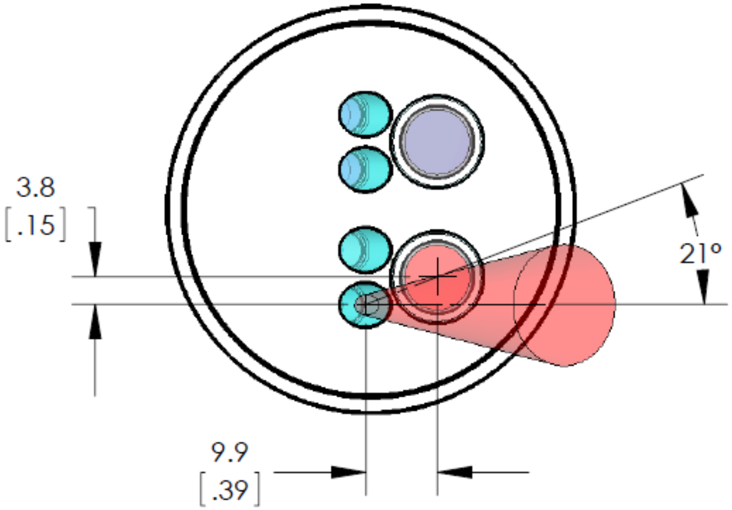
SECTION A-A
SCALE 2 : 1

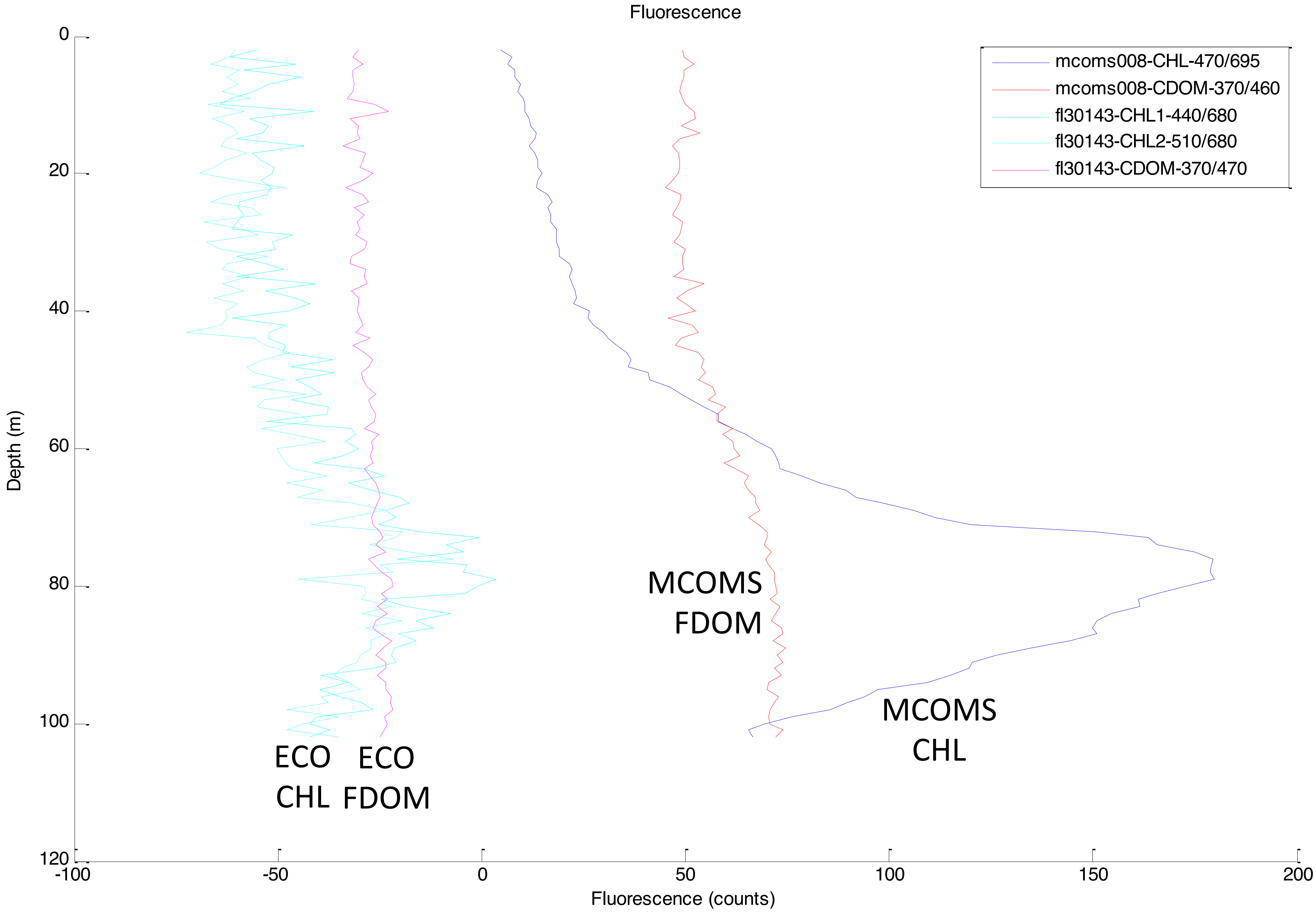
These angles are approximate.
- The detector has an epoxy dome that has some lensing effect.
- The filter loses efficiency as angle increases.



Actual light path (simulated in blue) is more complex than what I modeled.

SECTION B-B
SCALE 2 : 1

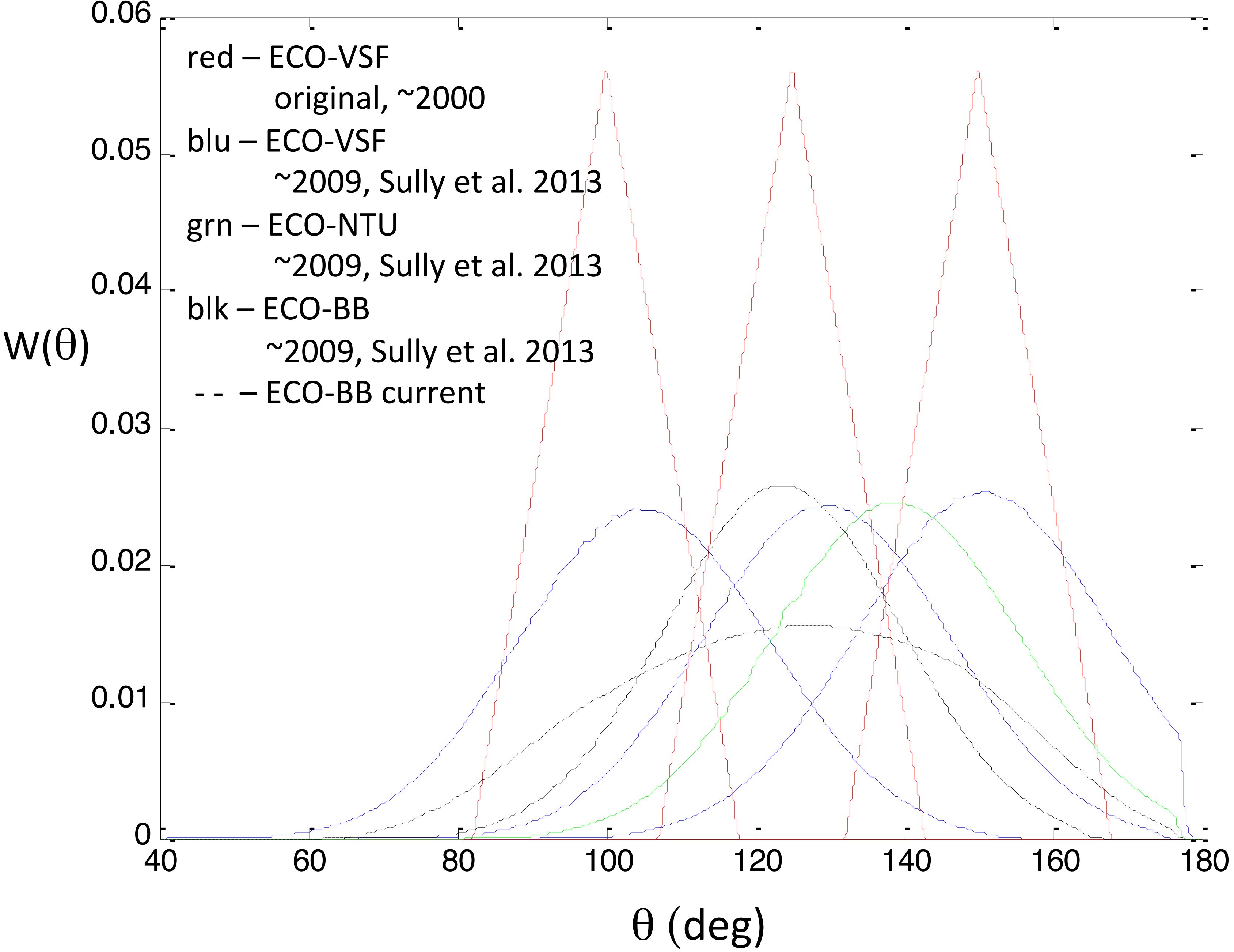


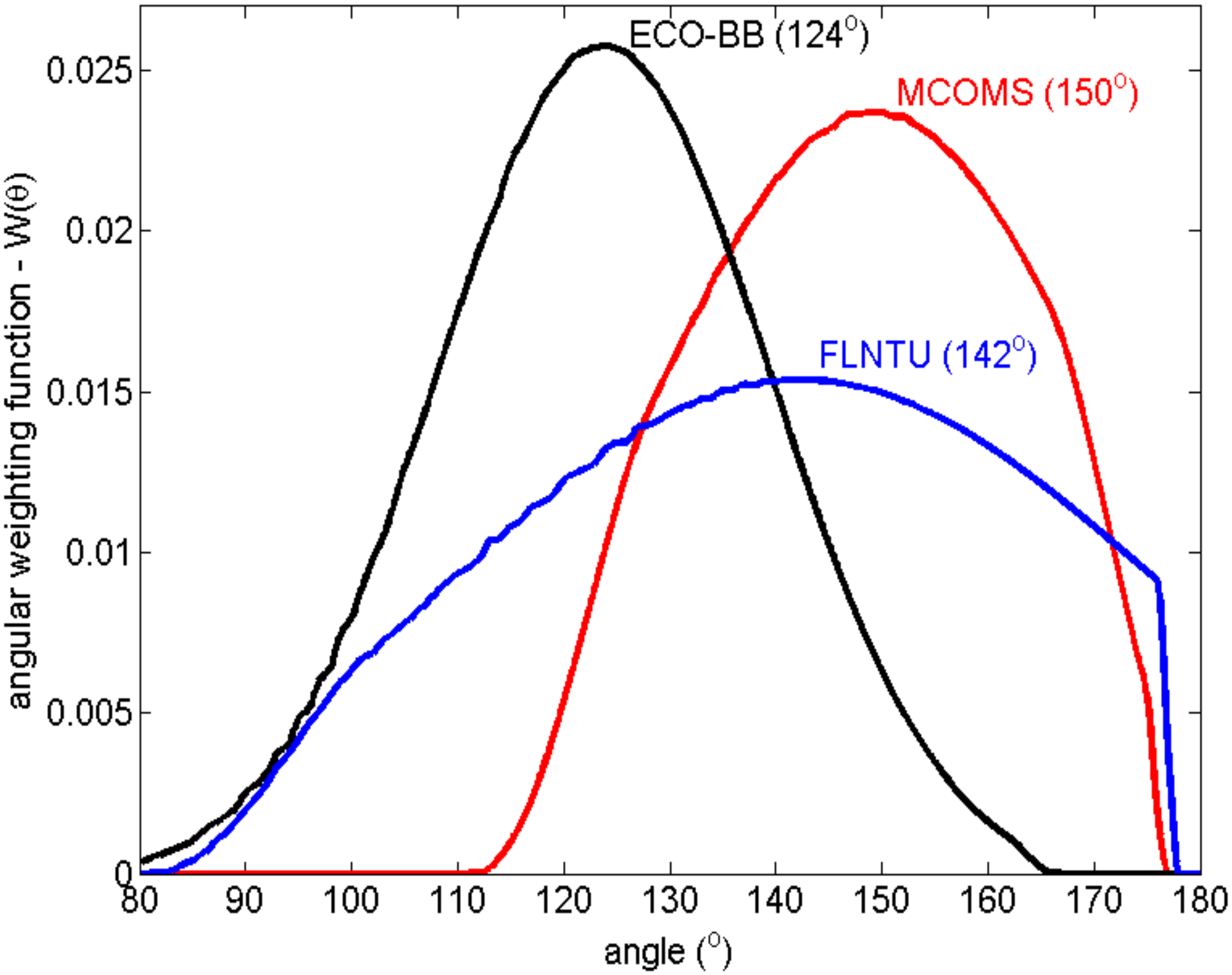

Fluorescence
0
20
40
60
80
100
120
Depth (m)
-100
-50
0
50
100
150
200
Fluorescence (counts)
mcoms008-CHL-470/695
mcoms008-CDOM-370/460
fl30143-CHL1-440/680
fl30143-CHL2-510/680
fl30143-CDOM-370/470
MCOMS FDOM
MCOMS CHL
ECO CHL
ECO FDOM

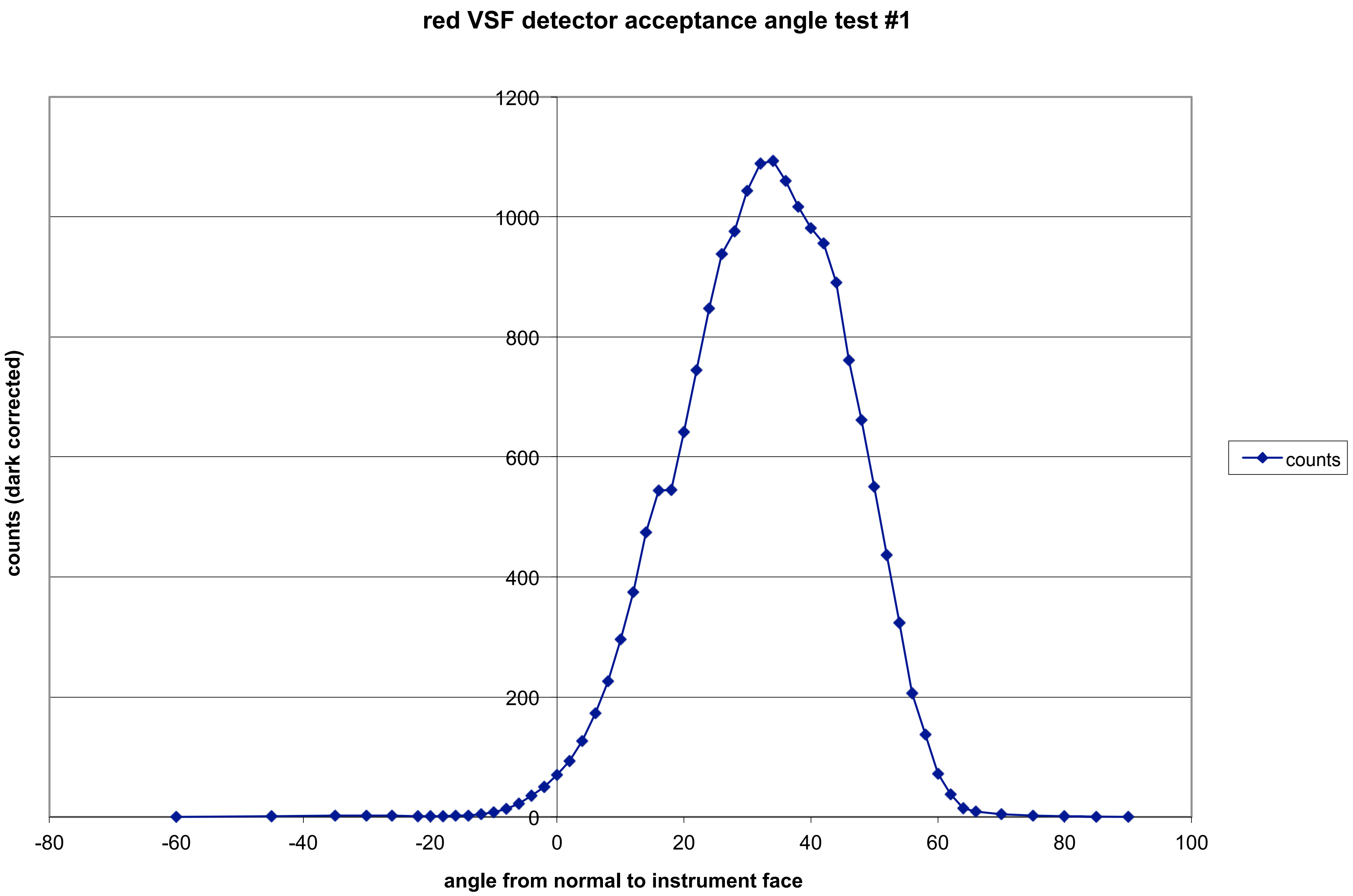
Comments on computing $W(\theta)$

- Need to set upper z limit when sample volume is theoretically infinite, or max z is very large (>= 25 cm typically suitable)
- Suitable Δx, Δy, and Δz typically <= 50 μm
- Need to apply Gaussian intensity distributions to both source and detector beams, with specified edge/peak
- Centroid theta of *W* is not the scattering angle computed from the center of the source and detector beams
- Effective sample volume determined by collective volume from where 99% (arbitrary) of detected signal emerges
  - Dependent on VSF, thus particle field, particle distributions…
- Effective pathlength defined by centroid theta of *W*

ECO weighting function history

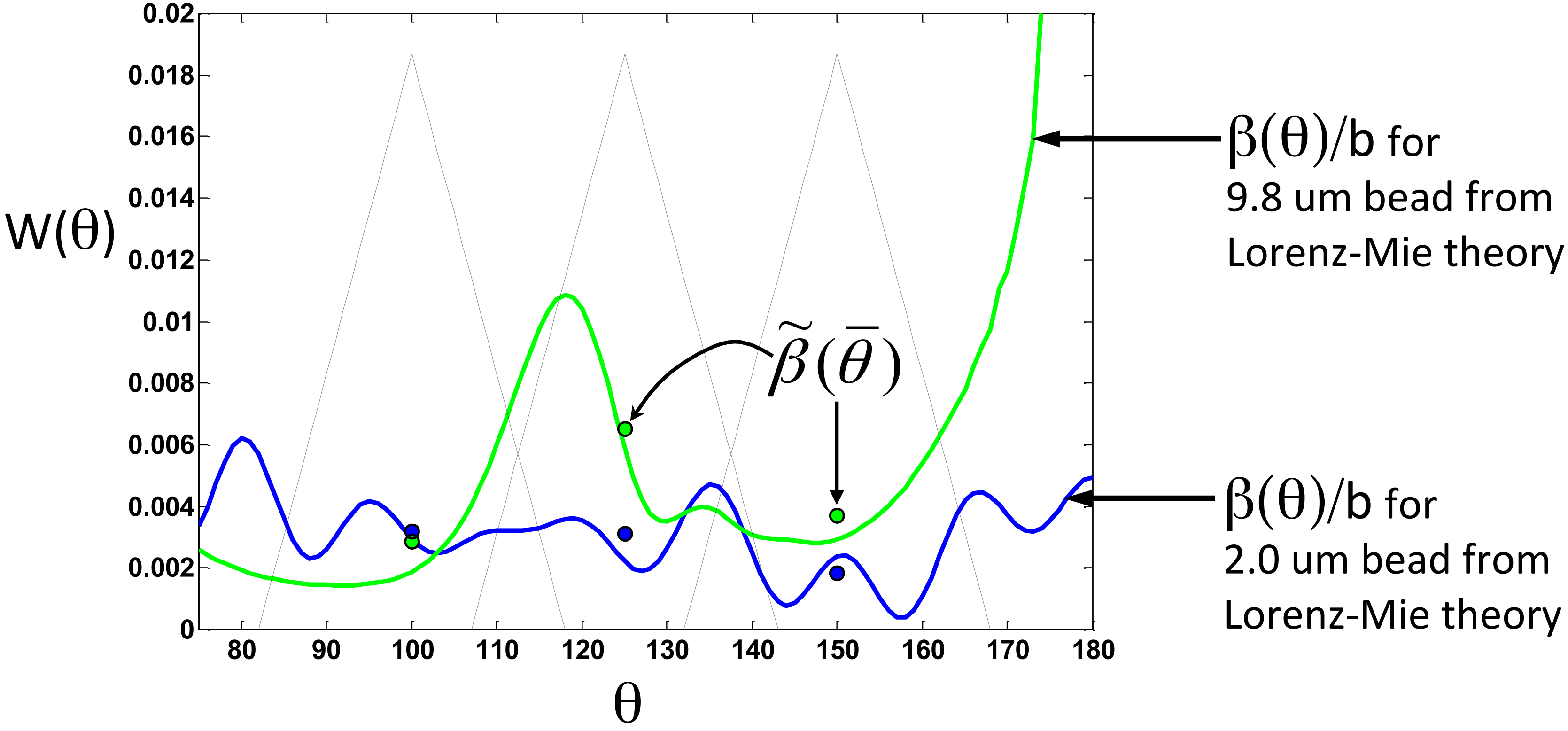



ECO-BB (124°)
MCOMS (150°)
FLNTU (142°)
angular weighting function - W(θ)
0.025
0.02
0.015
0.01
0.005
0
80
90
100
110
120
130
140
150
160
170
180
angle (°)


red VSF detector acceptance angle test #1
counts (dark corrected)
1200
1000
800
600
400
200
0
-80
-60
-40
-20
0
20
40
60
80
100
angle from normal to instrument face
counts

Calibration: Step 1

Compute phase function of easily modeled particle solution (e.g., microspherical beads) and convolve with W(θ)



β(θ)/b for 9.8 um bead from Lorenz-Mie theory

β(θ)/b for 2.0 um bead from Lorenz-Mie theory

Use a Rayleigh scatterer (*d* < λ) for best results!

Comments on Calibration: Step 1

Refractive index of polystyrene beads (wavelength, in μm):

n_p = 1.5663 + 0.00785/(λ^2) + 0.000334/(λ^4) (from Duke Sci)

Refractive index of freshwater, T in °C (wavelength, in nm):

n_m=1.31405 - 2.02e-6*T^2 + (15.868 - 4.23e-3*T)*(λ*1000)^-1 ...
- 4.382e3*(λ*1000)^-2 + 1.1455e6*(λ*1000)^-3 (Quan and Fry)

The size *distribution* of the beads is important, i.e., if the bottle says 2.12 with 0.16 um std, the std is important; need to compute phase function for a spectrum of sizes around the mode and then Gaussian weight according to the PSD.

Must use NIST-traceable beads with precisely defined PSD for optimal accuracy (WET Labs uses non-NIST beads)

In backward direction, 100 nm beads optimize accuracy in estimated phase function values

Calibration: Step 1

The *FULL* computation of the phase function…

$$\frac{\beta_p(\bar{\lambda},\sigma_\lambda,\bar{\theta},\Delta\theta,\bar{d},\sigma_d)}{b_p(\bar{\lambda},\sigma_\lambda,\bar{d},\sigma_d)}=\frac{\int_0^{\pi}\int_{\bar{\lambda}-3\sigma_\lambda}^{\bar{\lambda}+3\sigma_\lambda}\int_{\bar{d}-3\sigma_d}^{\bar{d}+3\sigma_d}W(\theta,\bar{\theta},\Delta\theta)\Psi(\lambda,\bar{\lambda},\sigma_\lambda)\alpha(d,\lambda,n_p,\theta)F(d,\bar{d},\sigma_d)\,\mathrm{d}d\,\mathrm{d}\lambda\,\mathrm{d}\theta}{2\pi\int_{\theta_a}^{\pi}\int_{\bar{\lambda}-3\sigma_\lambda}^{\bar{\lambda}+3\sigma_\lambda}\int_{\bar{d}-3\sigma_d}^{\bar{d}+3\sigma_d}\sin(\theta)\Psi(\lambda,\bar{\lambda},\sigma_\lambda)\alpha(d,\lambda,n_p,\theta)F(d,\bar{d},\sigma_d)\,\mathrm{d}d\,\mathrm{d}\lambda\,\mathrm{d}\theta}$$

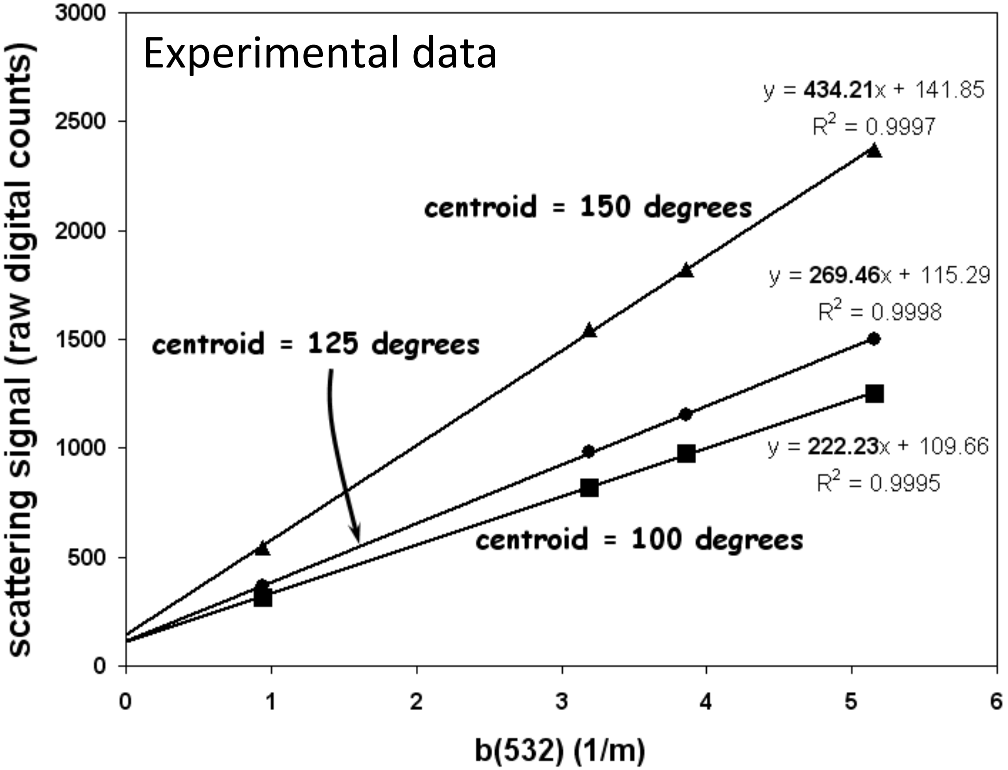
Ψ - the **spectral response** of the sensor, defined by a centroid wavelength and standard deviation σ_λ

α - amplitude of **unpolarized light scattering** by the microspheres calibration standard computed from Lorenz-Mie theory (Bohren and Huffman 1983)

F - **size distribution** of the microsphere standard defined by a centroid and standard deviation σ_d.

Calibration: Step 2

Place sensor in the solution with known phase function and measure raw digital counts and *b* (with ac9)



Intercepts are nonzero because

1) scattering sensor dark counts
2) ac9 is not calibrated precisely
3) insufficient water purity

<u>these do not matter</u> because the slope is what you care about, i.e., the change in counts per change in *b*

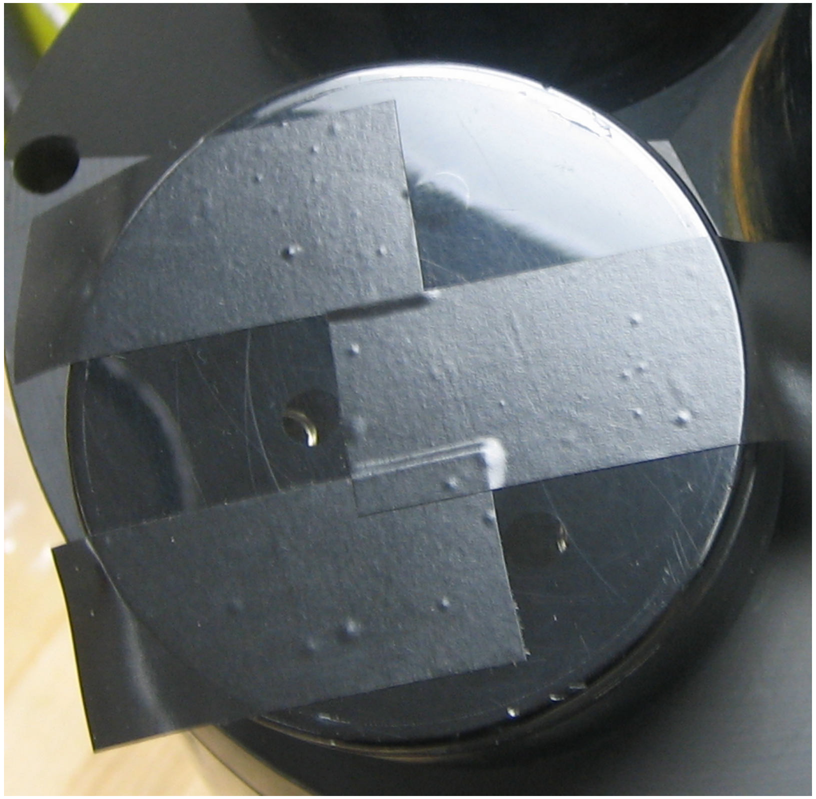
Calibration: Step 3

Compute scaling factor, SF

$$SF = \frac{\beta(\bar{\theta})}{\underset{\substack{\uparrow \\ \text{theory}}}{b}} \, \frac{\overset{\substack{\text{experimental} \\ \downarrow}}{b}}{counts} = \frac{\beta(\bar{\theta})}{counts}$$

Calibration: Step 4

Determine dark offset, DO



- -black tape over detector only
- -put in water to match refractive index
- -average time record (~30 s)

Applying the calibration

$$\beta(\overline{\theta}) = \begin{matrix}\text{scaling}\\ \text{factor}\end{matrix}\left(\begin{matrix}\text{raw}\\ \text{counts}\end{matrix} - \begin{matrix}\text{dark}\\ \text{offset}\end{matrix}\right)$$

Important…

- All $\beta(\theta)$ measurements are not equal due to instrument-specific $W(\theta)$
- Measurements of $\beta(\theta)$ in the field ***will include water***. Calibration is to signal response due to adding particles of known scattering properties, with dark offset providing baseline. There is no purified water subtraction, as water from standard polishing systems is not close to being clean enough (pure water itself is several counts of signal)
- Ambient light rejection circuitry important for backscattering measurements

Correction for attenuation

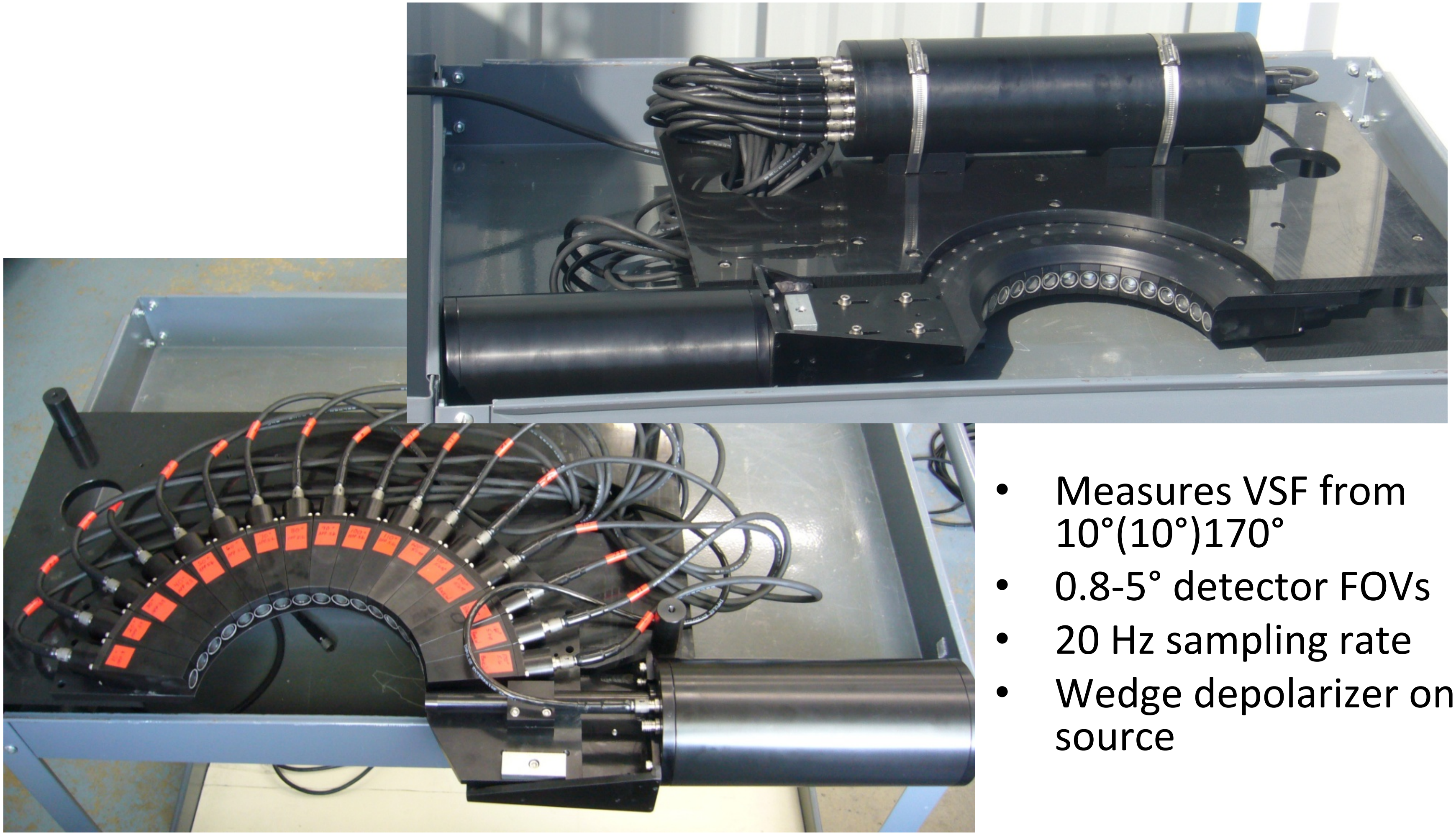
Required because light is attenuated on its way to and from the sample volume

For bead calibration, scattering portion of attenuation is inherently corrected (close enough for ECOs…); only need to correct for absorption when absorption is extremely high (> ~2 1/m):

$$\beta_{corr} = \beta_{meas} \exp(aL)$$

<u>This is an approximation, valid when pathlength L is small</u>

When pathlength is not small: MASCOT
(Multi-Angle SCattering Optical Tool)

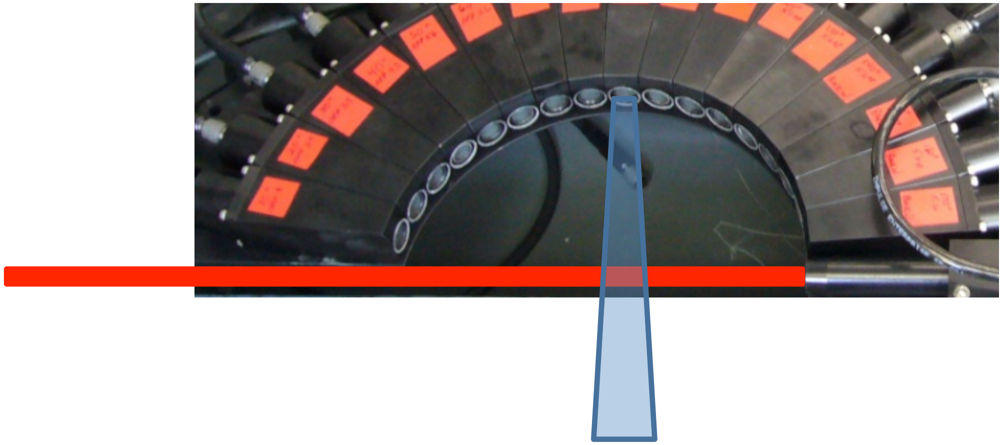


- Measures VSF from 10°(10°)170°
- 0.8-5° detector FOVs
- 20 Hz sampling rate
- Wedge depolarizer on source

Full correction for attenuation

$$\beta(\bar{\theta}_i) = \frac{R_{cal}}{R_m}[\Phi_i - D_i]f_i e^{L[b_p\varepsilon + a_{pg} + a_w]}$$

R – source references
ε – fraction of scattering that is not included in the measurement



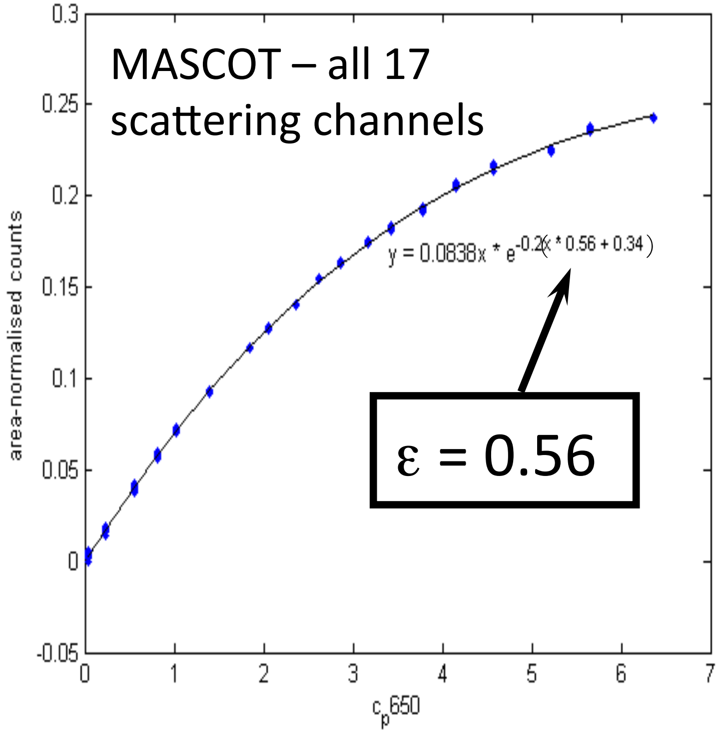
L ~ 20 cm

Twardowski et al. (2012)

Full correction for attenuation

Can solve for ε empirically…

$$\boxed{[\Phi(\theta) - DO(\theta)] \propto b_p \exp[-L * (b_p * \varepsilon + a_t)]}$$


MASCOT – all 17 scattering channels

$\varepsilon = 0.56$

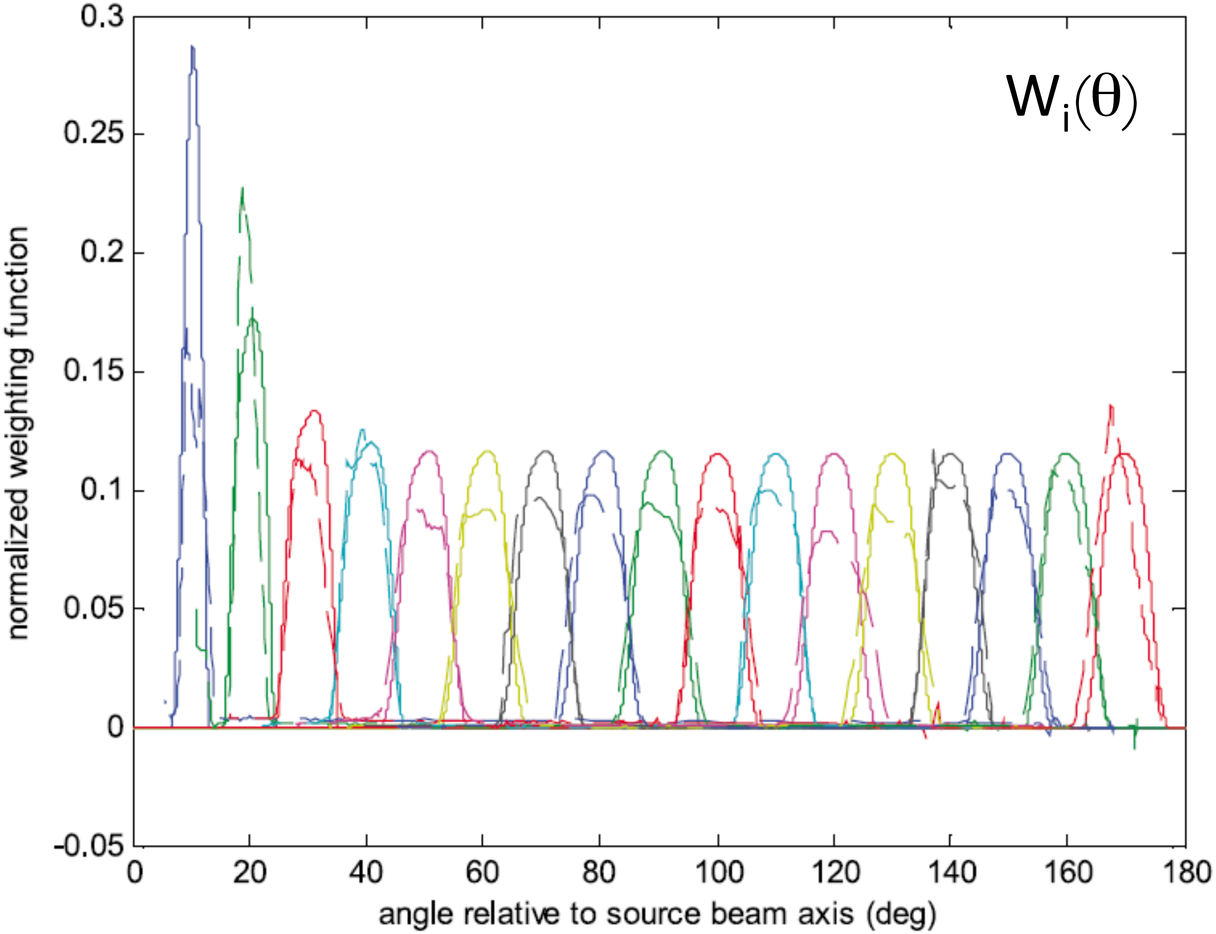
Arizona Road Dust

(similar VSF to oceanic VSFs)

- detector field-of-view unimportant (detector footprint *is* important)
- scaling factor (*f*) is irrelevant, only interested in shape of response
- ε dependent on phase function shape

Twardowski et al. (2012)

MASCOT cals: theoretical part I



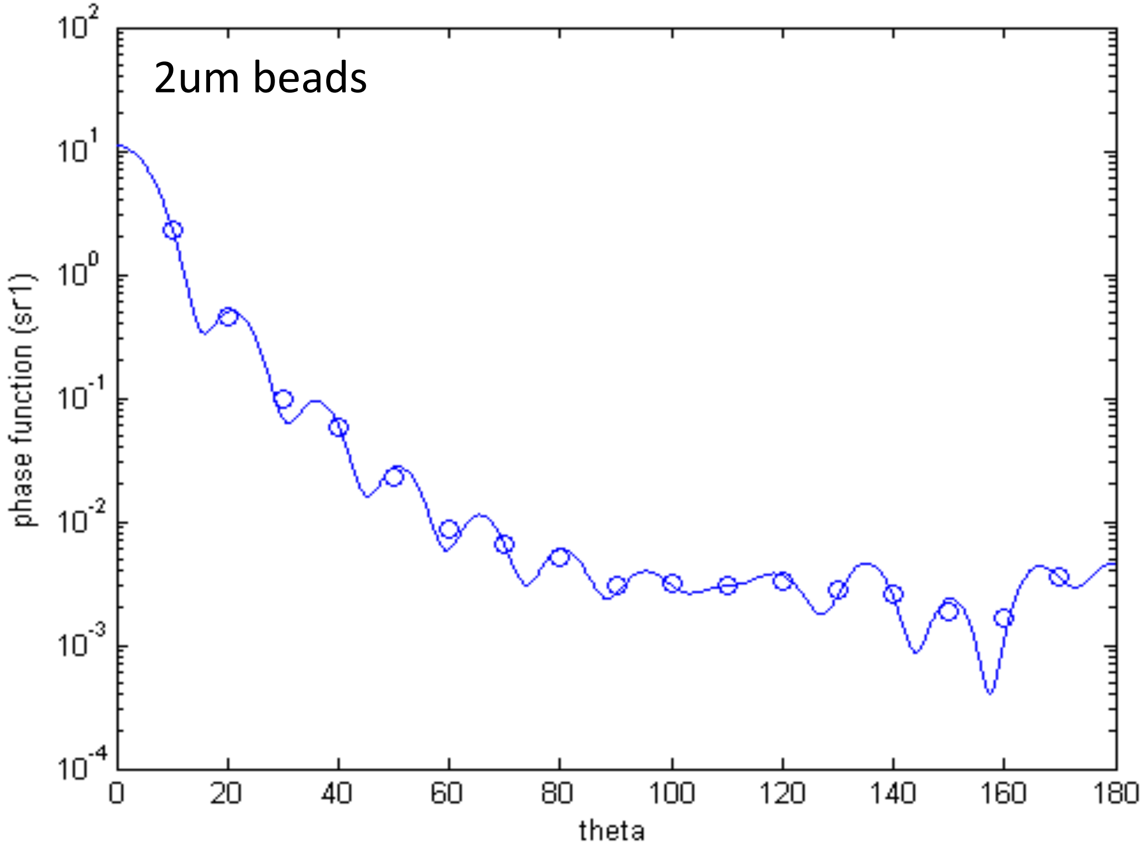
Derive $W(\theta)$

Figure A2. Angular weighting functions for the 17 MASCOT VSF channels. Solid traces were computed numerically, and dotted traces were derived from lab measurements in air.

Twardowski et al. (2012)

MASCOT cals: theoretical part II

Compute phase function of easily modeled particle solution (e.g., microspherical beads) and convolve with W(θ)



Twardowski et al. (2012)

MASCOT cals: empirical part

$$\beta(\bar{\theta}_i) = \frac{R_{cal}}{R_m}[\Phi_i - D_i] f_i e^{L[b_p \varepsilon + a_{pg} + a_w]}$$

Need to solve for scaling factor, f

Rearrange, add phase function P (get rid of *R* coefficients…)

$$\boxed{[\Phi(\theta) - DO(\theta)] = b_p * [P(\theta)/f(\theta)] * \exp[-L * (b_p * \varepsilon + a_t)]}$$

- plot counts vs b_p for bead solution suspension series
- fit the above equation, solving for *f*
- note specific ε for specific bead solution must be used
- suspension series kept dilute to minimize path attenuation
- signal for forward angles very low for Rayleigh scatterers; optimal to use larger bead size for those angles

Twardowski et al. (2012)

Polarized scattering

VSF shape

V, H linear polarization

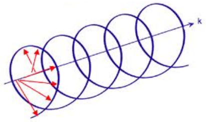
particle orientation

$$\begin{pmatrix} I_s \\ Q_s \\ U_s \\ V_s \end{pmatrix} = \frac{1}{k^2 r^2} \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{pmatrix} \begin{pmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{pmatrix}$$

total intensity

⊕

⊗



SCATTERED BEAM

particle nonsphericity

INCIDENT BEAM

(θ, λ)

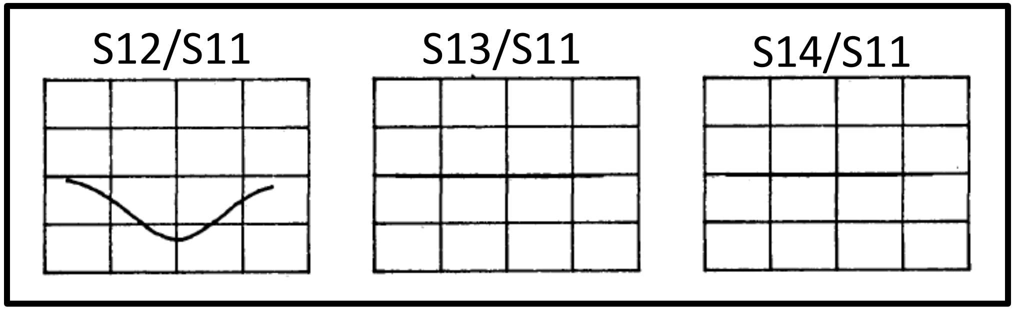
Mueller matrix
(a “scattering event”)

Voss and Fry (1984): Mueller matrix
MASCOT: POLIMOD

Degree of Linear Polarization

DoLP = -S12 / S11
= -(H-V)/(H+V)

H = ½(S11 + S12)
V = ½(S11 – S12)



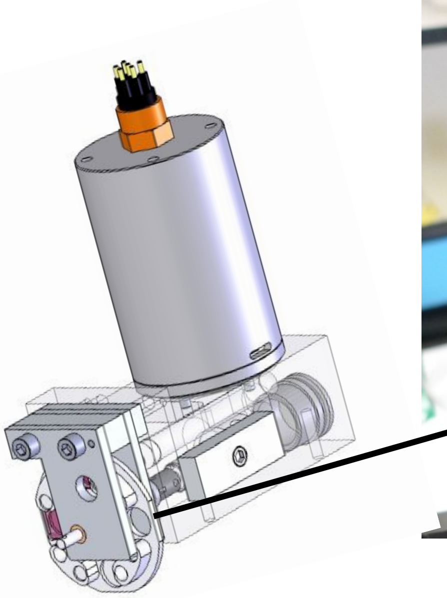
4 positions

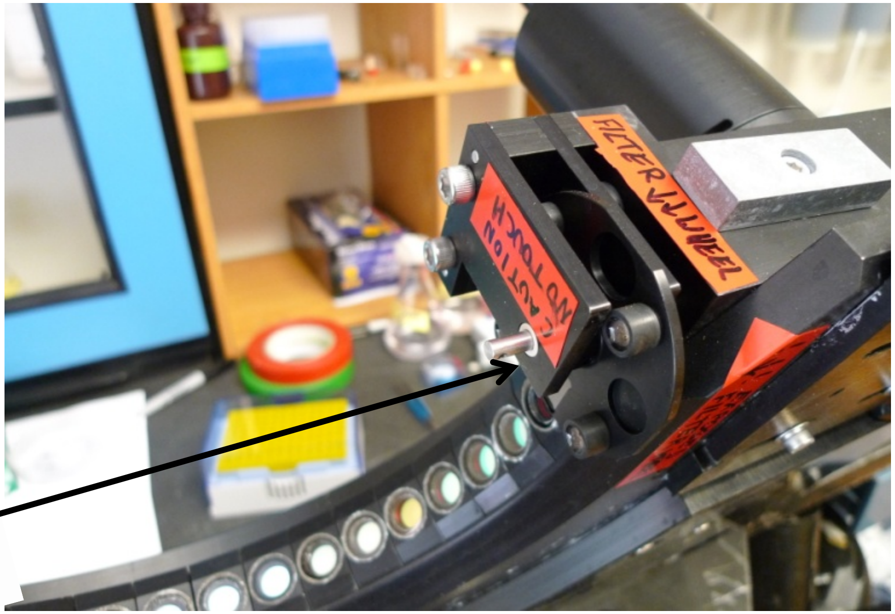
1 - OPEN

2 - DARK

3 - H ↔

4 - V ↕





"Average" for Atlantic and Pacific Oceans (bench measurements)
(*only published matrix for bulk ocean water…*)

Measuring polarization

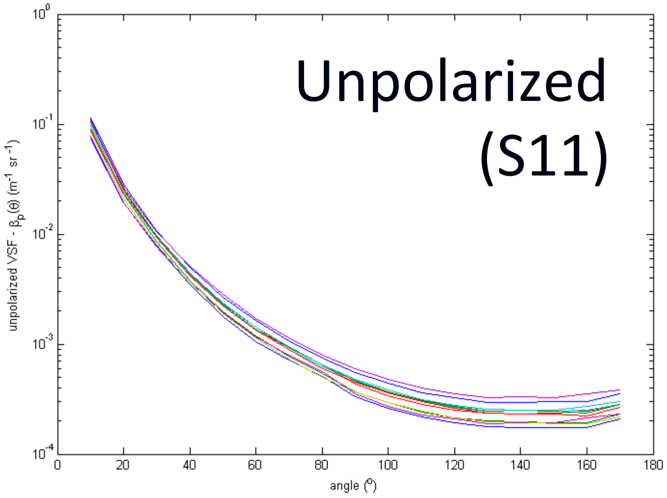
linear	*oblique linear*	*circular*
Measuring S12	Measuring S13	Measuring S14
$H = ½(S11 + S12)$ $V = ½(S11 – S12)$	$O_+ = ½(S11 + S13)$ $O_- = ½(S11 – S13)$	$R = ½(S11 + S14)$ $L = ½(S11 – S14)$
$-S12 / S11 = -(H-V)/(H+V)$	$-S13 / S11 = \frac{-(O_+ - O_-)}{(O_+ + O_-)}$	$-S14 / S11 = -(R-L)/(R+L)$
$S12 = H-V$ *and* $S11 = H+V$	$S13 = O_+ - O_-$ *and* $S11 = O_+ + O_-$	$S14 = R-L$ *and* $S11 = R+L$

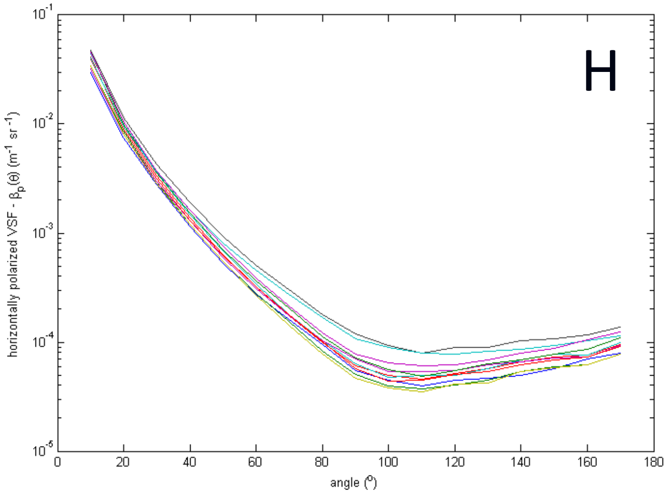
- *however, there are transmission losses due to the filters (~90% T)*
- *ratiometric values are fine, as transmission factor cancels*

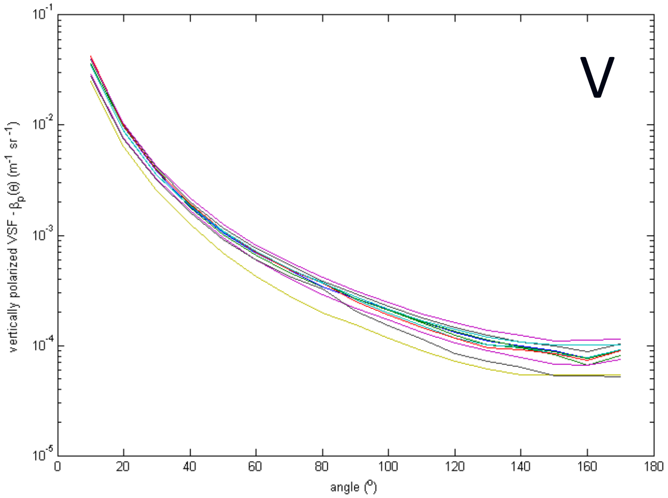
“true” $S11 = (H + V)/T$ (*where $T = 0.9$*)

S11 can be validated with direct open path measurement

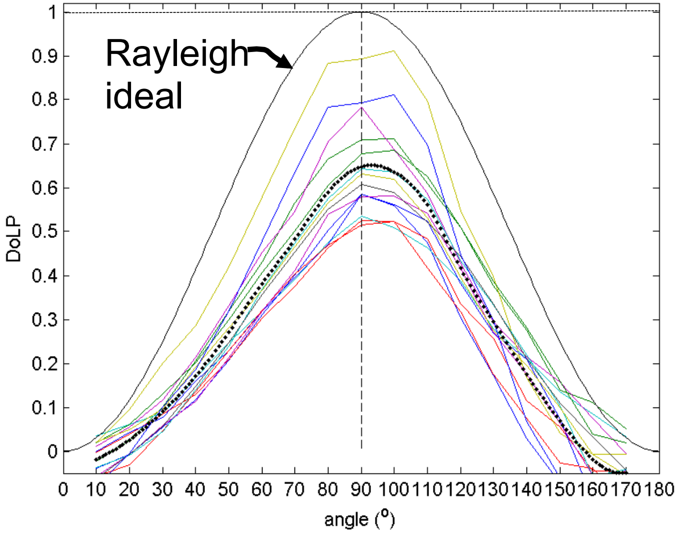
Curaçao, 2012: single vertical profile





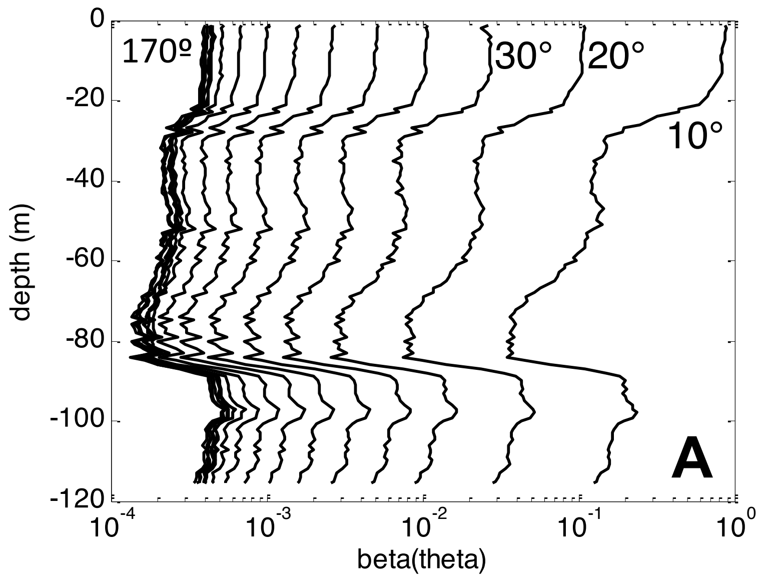


DoLP $= -S_{12} / S_{11} = -(H-V)/(H+V)$

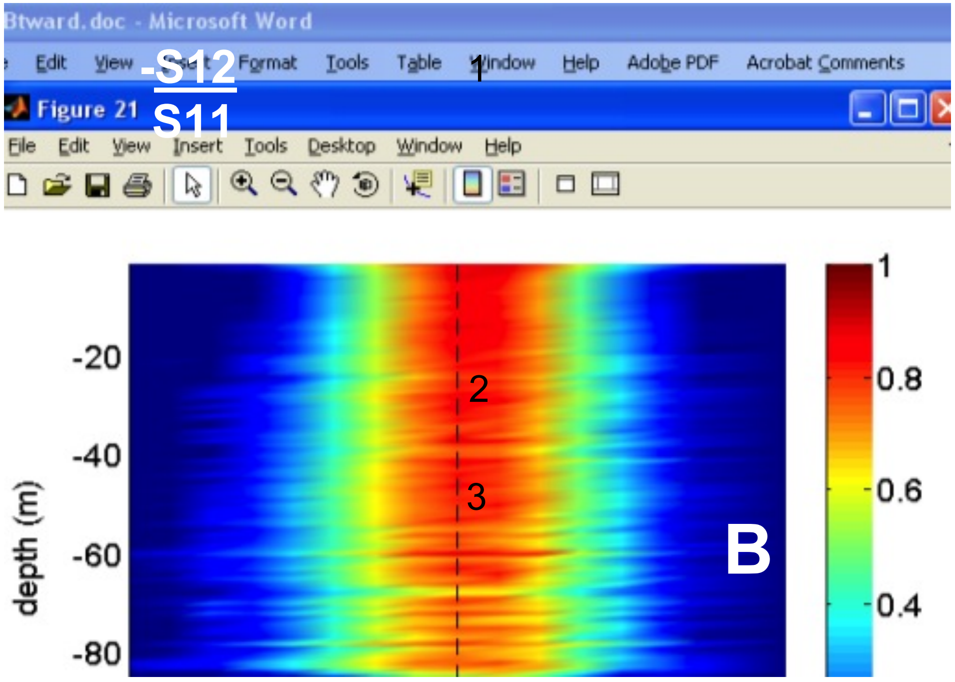


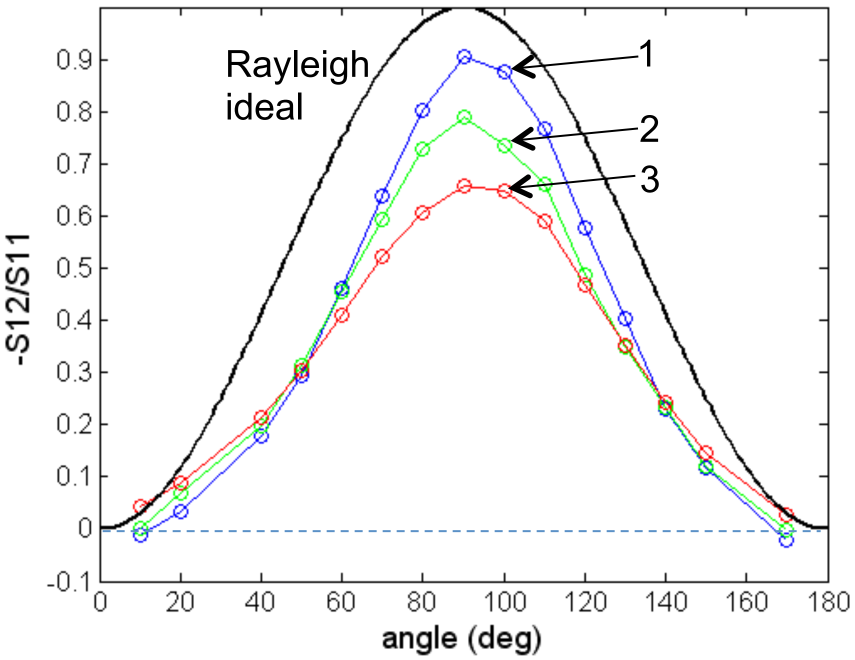
This is the first time these measurements have been made in situ

Santa Barbara Channel 2008

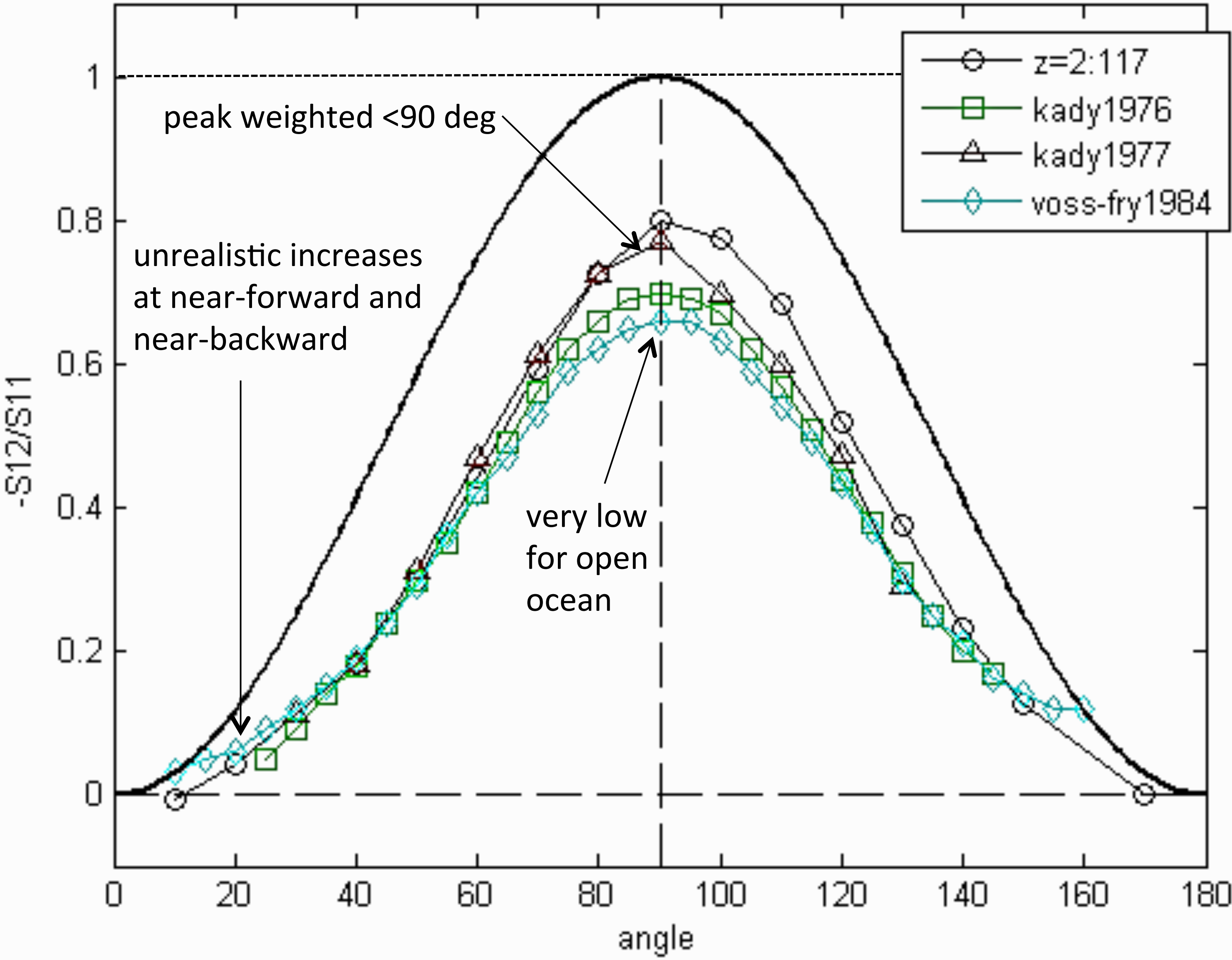


MASCOT VSF profile





Santa Barbara Channel -- Sep 10, 2008



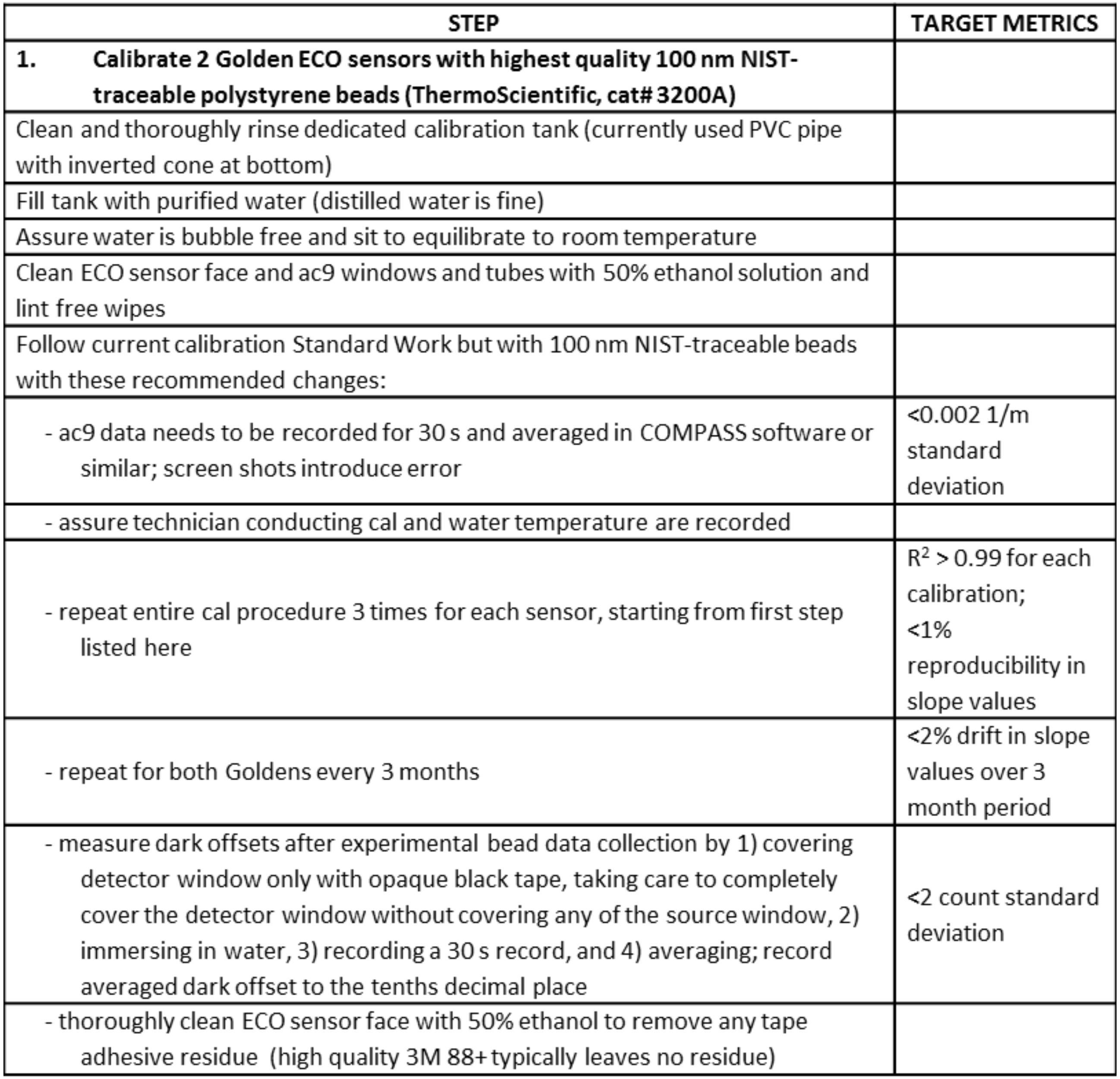
peak weighted <90 deg

unrealistic increases at near-forward and near-backward

very low for open ocean

Only other S12/S11 functions ever published for whole SW

Vicarious ECO calibration option



STEP	TARGET METRICS
1. Calibrate 2 Golden ECO sensors with highest quality 100 nm NIST-traceable polystyrene beads (ThermoScientific, cat# 3200A)	
Clean and thoroughly rinse dedicated calibration tank (currently used PVC pipe with inverted cone at bottom)	
Fill tank with purified water (distilled water is fine)	
Assure water is bubble free and sit to equilibrate to room temperature	
Clean ECO sensor face and ac9 windows and tubes with 50% ethanol solution and lint free wipes	
Follow current calibration Standard Work but with 100 nm NIST-traceable beads with these recommended changes:	
- ac9 data needs to be recorded for 30 s and averaged in COMPASS software or similar; screen shots introduce error	<0.002 1/m standard deviation
- assure technician conducting cal and water temperature are recorded	
- repeat entire cal procedure 3 times for each sensor, starting from first step listed here	R^2 > 0.99 for each calibration; <1% reproducibility in slope values
- repeat for both Goldens every 3 months	<2% drift in slope values over 3 month period
- measure dark offsets after experimental bead data collection by 1) covering detector window only with opaque black tape, taking care to completely cover the detector window without covering any of the source window, 2) immersing in water, 3) recording a 30 s record, and 4) averaging; record averaged dark offset to the tenths decimal place	<2 count standard deviation
- thoroughly clean ECO sensor face with 50% ethanol to remove any tape adhesive residue (high quality 3M 88+ typically leaves no residue)	

Vicarious ECO calibration option (cont.)

2. Vicariously calibrate Production ECOs in a suspension series of Arizona Test Dust (Powder Technologies, ATD Ultrafine 12103-1)	
Use tank of same design as bead calibration tank, but dedicate this tank to Production ECO calibrations .	
Clean and thoroughly rinse calibration tank.	
Fill tank with purified water (distilled water is fine)	
Assure water is bubble free and sit to equilibrate to room temperature	
Use 5 suspensions (initially) of ATD covering a similar dynamic range as bead calibrations (up to 80% of full dynamic range). Continually circulate tank water with a vigorously rotating matte black stir bar. Pump could be used (intake and outtake at top and bottom of tank, respectively) as long as any bubble generation from entrained air and/or from cavitation can be completely avoided.	
Collect measurements with Golden #1 and Production ECO in each suspension	
Obtain scaling factor directly from linear least-squares fit of counts vs Golden#1 VSF (1/m-sr)	$R^2 > 0.99$
For last suspension, also measure with Golden #2 for validation point	<2% agreement between Goldens
Measure dark offset (for both Golden units and calibrated sensor) after experimental ATD data collection by 1) covering detector window only with opaque black tape, taking care to completely cover the detector window without covering any of the source window, 2) immersing in water, 3) recording a 30 s record, and 4) averaging; record averaged dark offset to the tenths decimal place	<2 count standard deviation
Thoroughly clean ECO sensor face with 50% ethanol to remove any tape adhesive residue (high quality 3M 88+ typically leaves no residue)	

Vicarious ECO calibration: benefits

- All ECO scattering measurements would be **NIST traceable**
- **More accurate** (more than 5% (>2X) improvement) because Reference Sensor calibration would be carried out with 0.1 um NIST traceable beads instead of 2 um non-NIST traceable beads (note that 2 um beads are used now because far less bead solution is required to obtain a calibration, reducing cost)
- **Less expensive** because very cheap AZRD now used for calibration instead of beads every time
- **Better reproducibility** because all Production sensors would be calibrated to a single Reference Sensor
- **Less opportunity for error** because the procedure is far more simple
- **Less labor intensive**, i.e., quicker and requires less expertise
- **Less asset intensive** since no concomitant ac-9 measurements would be required

b_b sensor concept from Ed Fry's lab

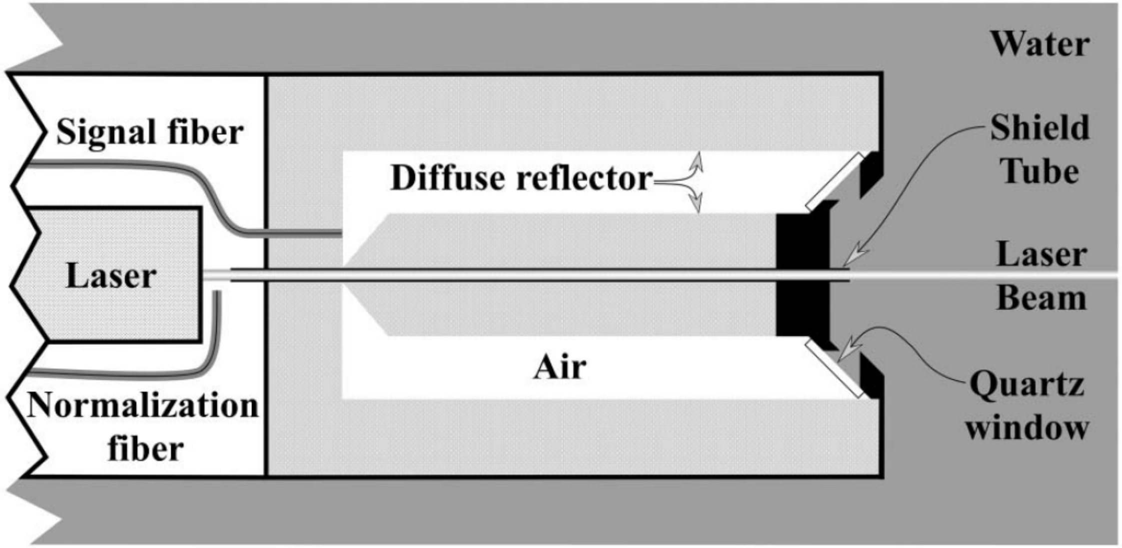
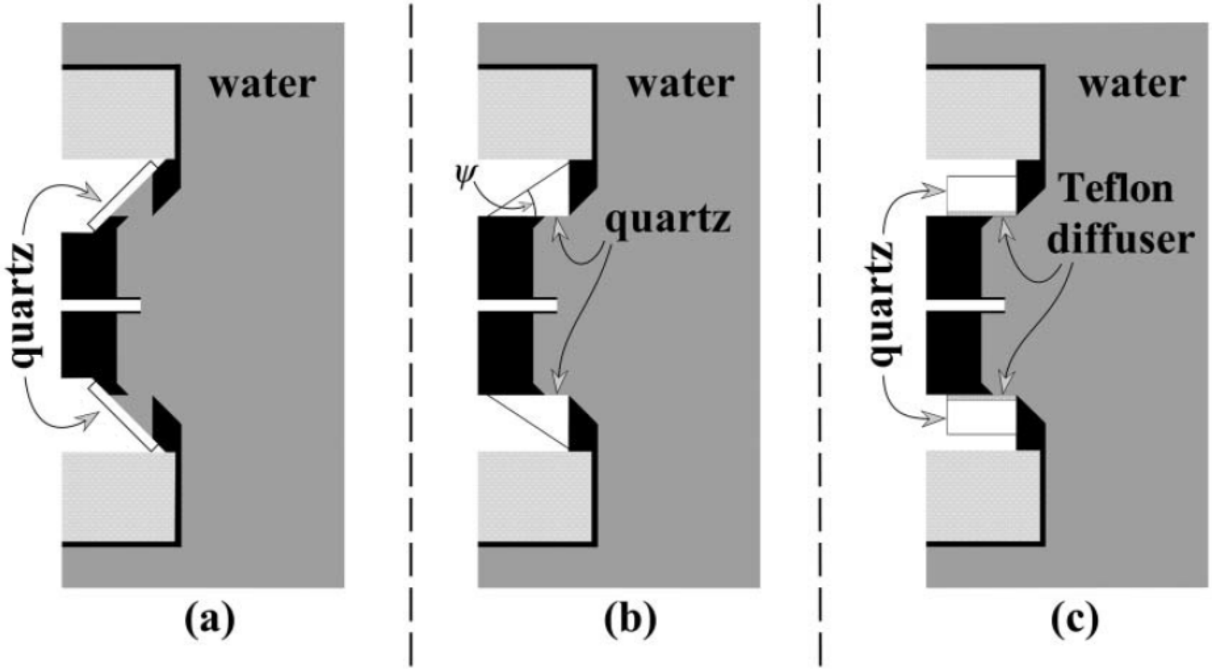
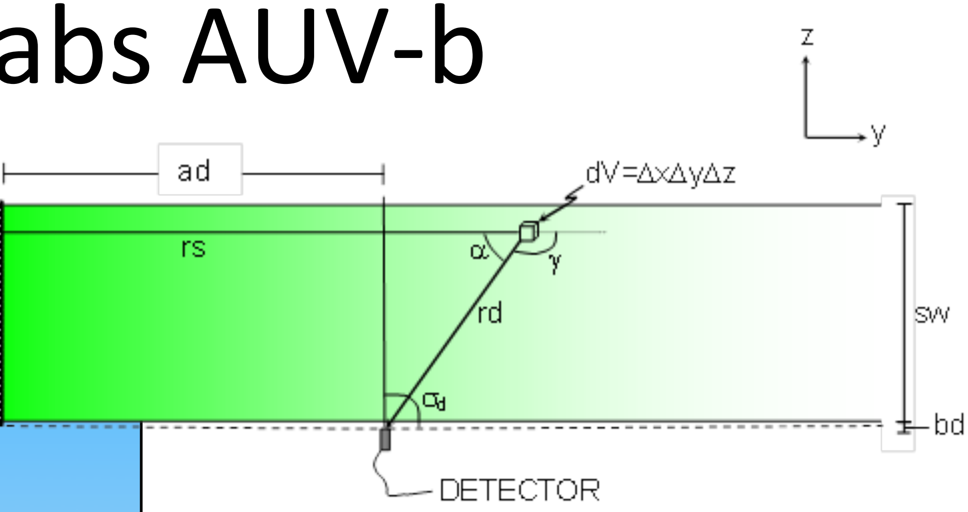


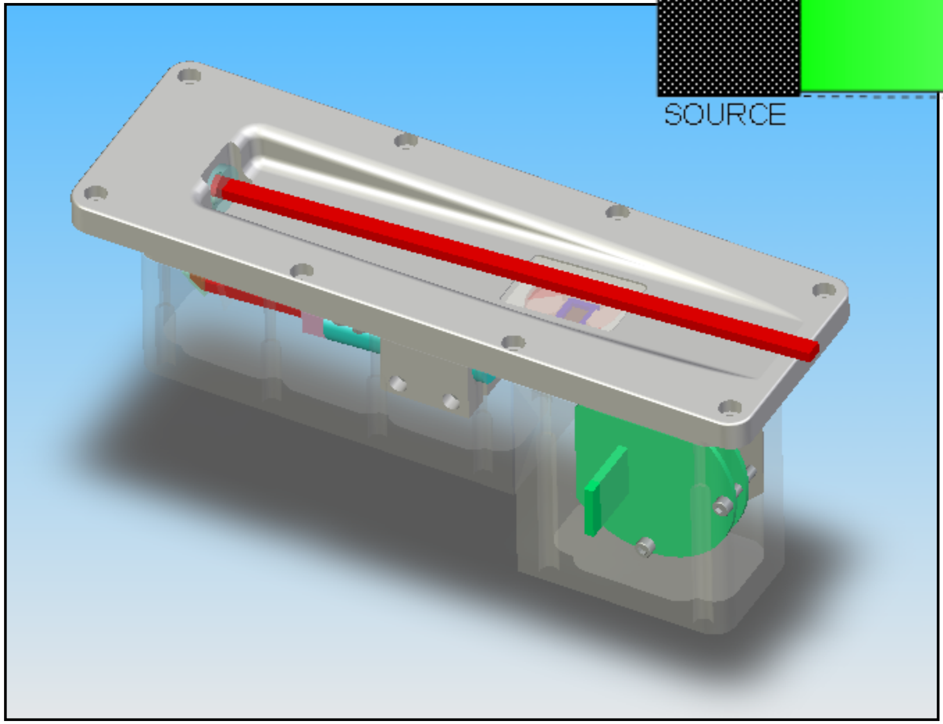
Fig. 8. Instrument implementation—cylindrical symmetry around laser beam (except for fibers).



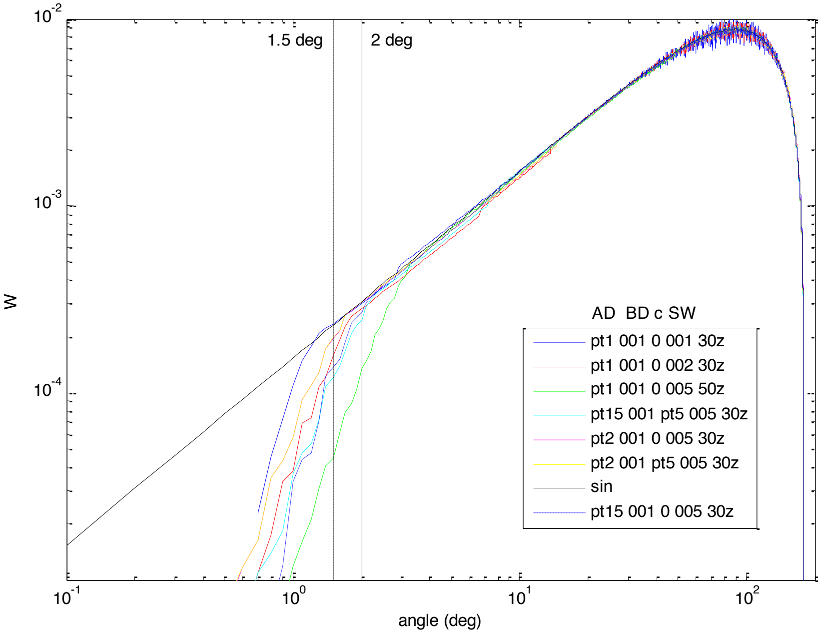
Haubrich et al. (2011)

WET Labs AUV-b

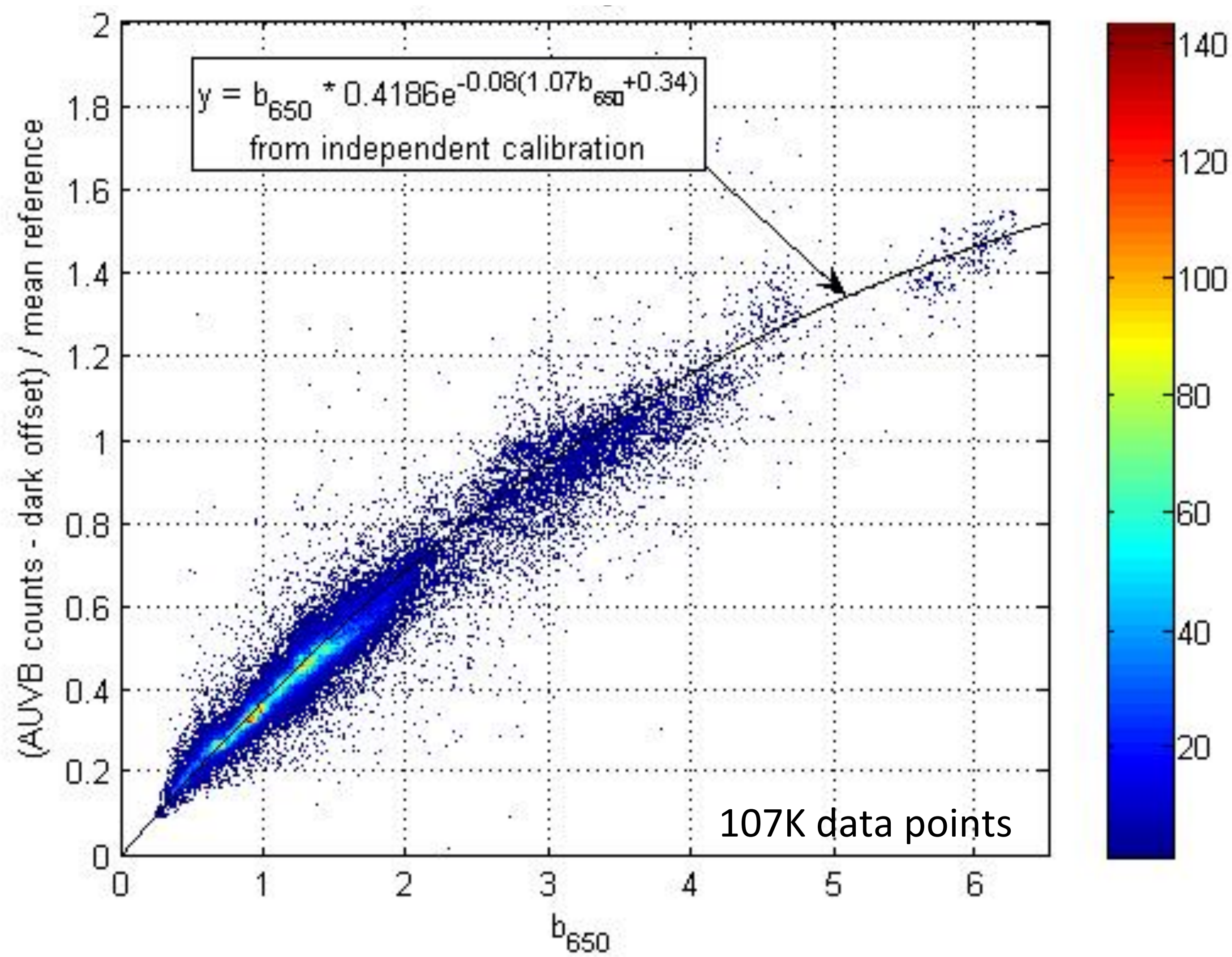




Twardowski et al. (unpub, 2006-2010)

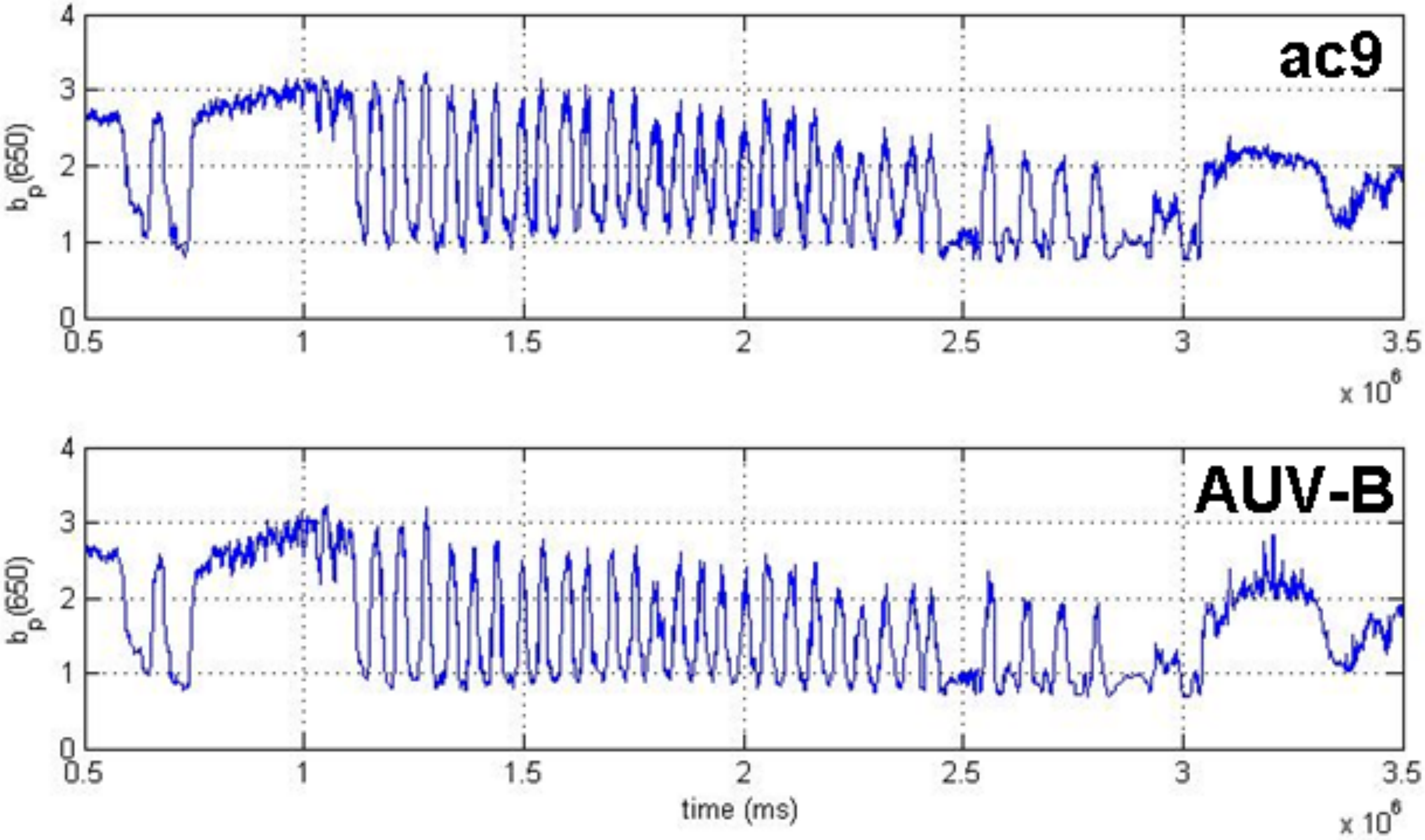


AUV-b validation with ac9



107K data points

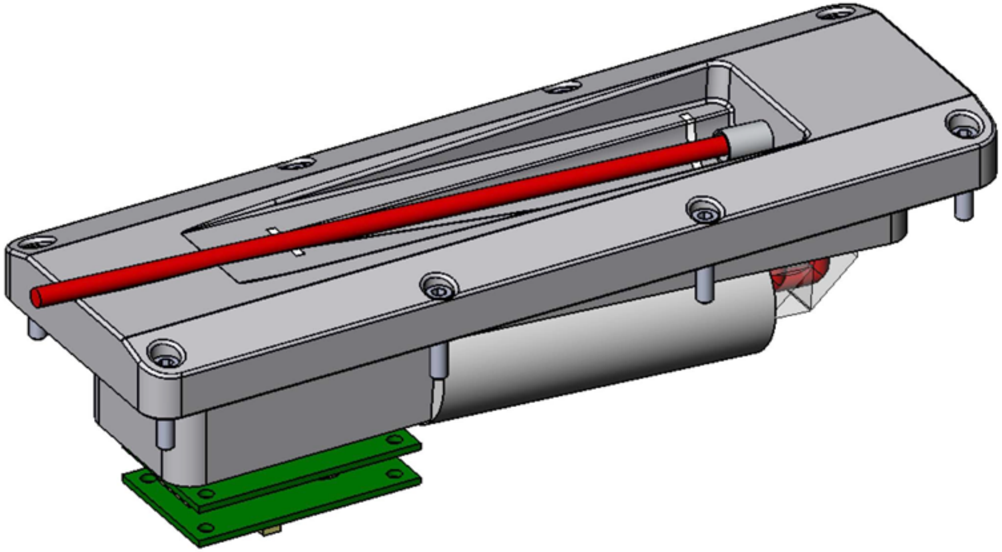
ac9 comparison

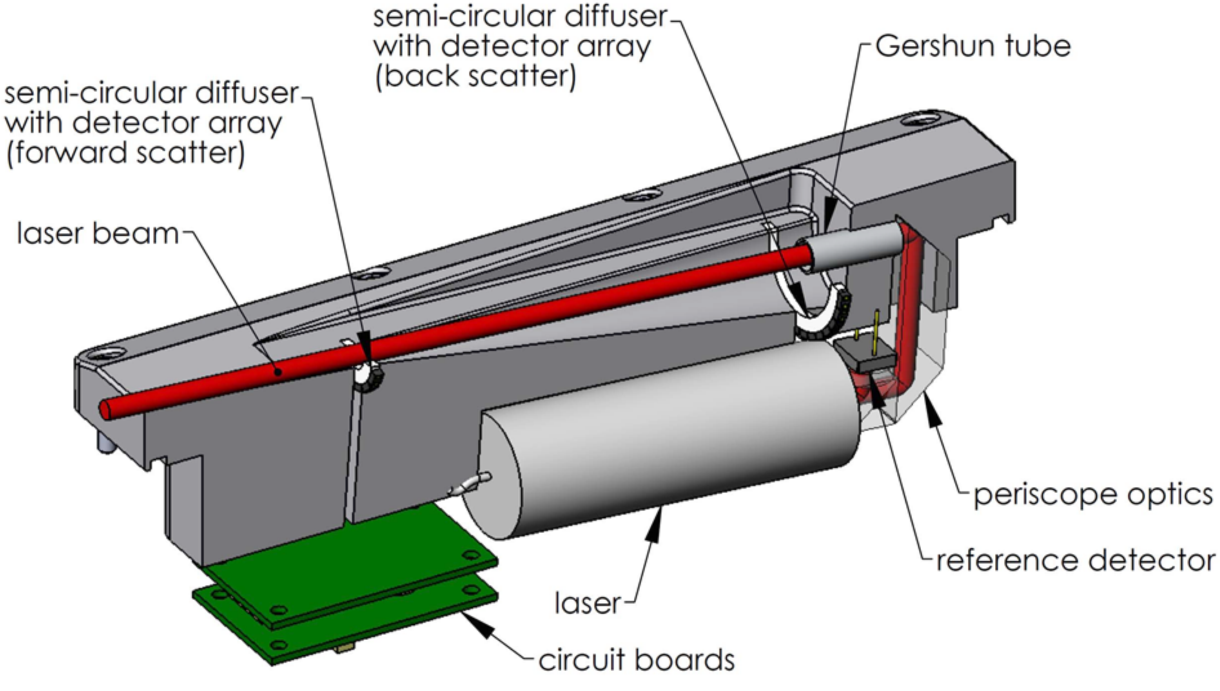


bb-b sensor

NSF OTIC

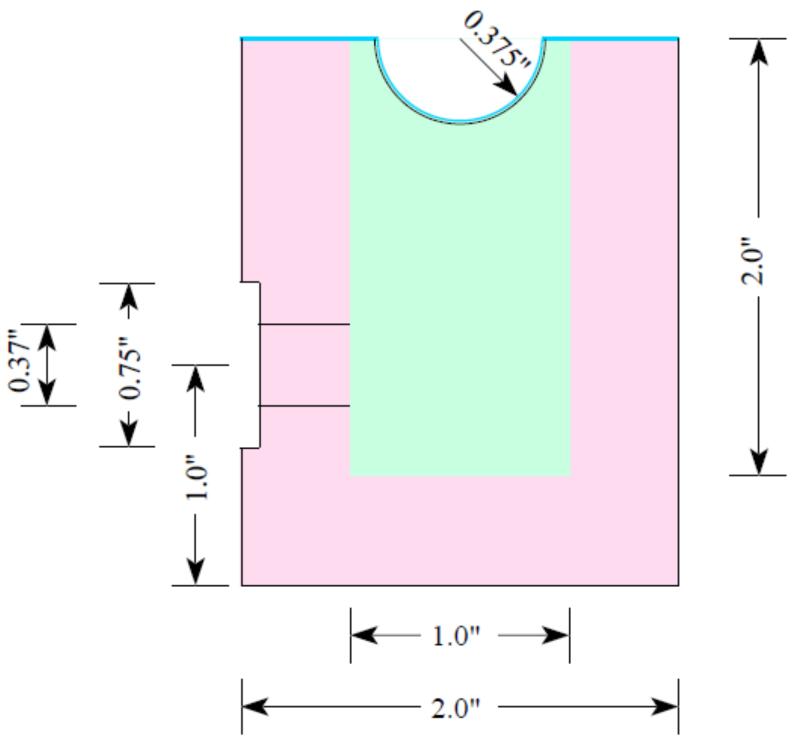
Fry-Twardowski





The hard part: constructing an adequate cosine collector

Cross-section through the middle



Orthogonal cross-section through the middle