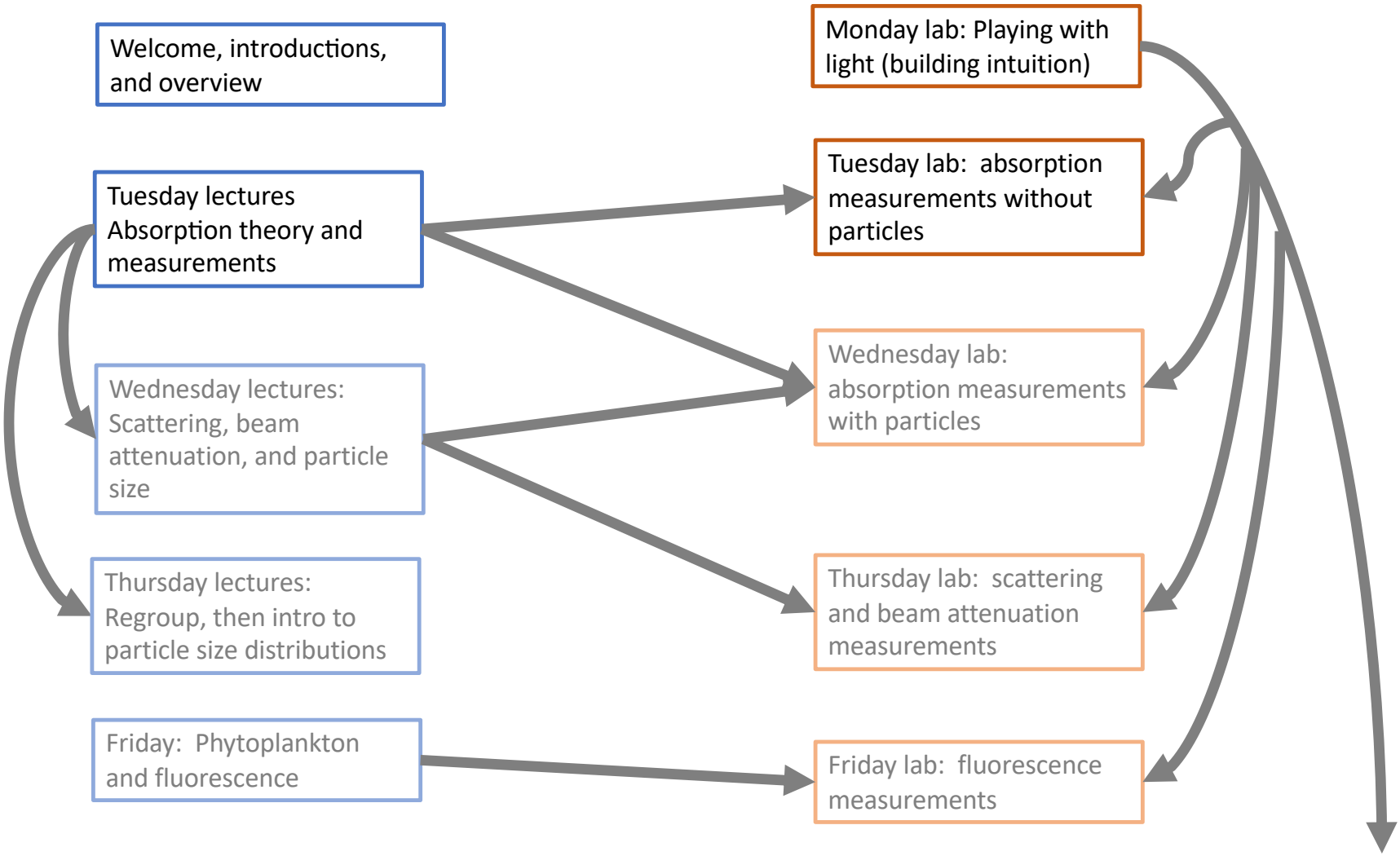
Class context: Week 1 roadmap – Inherent optical properties



Absorption, part 2

- Beer-Lambert-Bouguer Law
  - Conceptual
  - Realistic
- Survey of measurement techniques
- Lab overview

Beer's Law

... or Beer-Lambert-Bouguer law – see Mobley et al. 2022, p. 357 footnote for historical dates

- Bouguer and Lambert: Light decays exponentially through a medium

$$L(r) = L(0)e^{-a(r)}$$

where *L* is the radiance, *r* the pathlength, and *a* is the absorption coefficient.

- Beer: The decay coefficient of the exponential decrease is proportional to the concentration of the absorbing substance

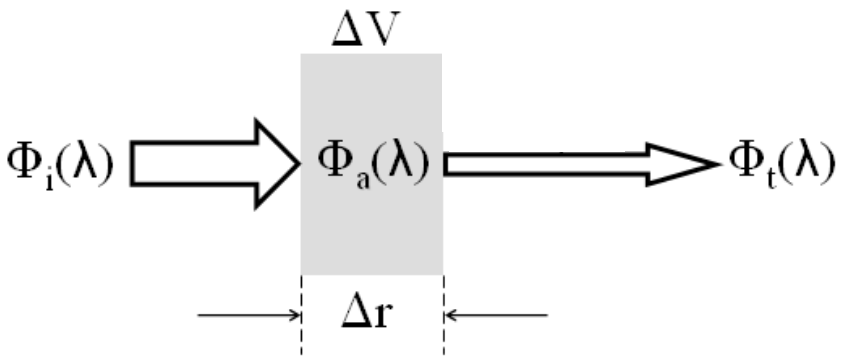
$$a = a^* \times C$$

where a^* is the concentration-specific absorption coefficient and *C* is the concentration of the absorbing substance.

- If there are multiple absorbing substances, we can simply sum them up:

$$a = \sum_i a_i^* \times C_i$$

Deriving Beer's Law



Consider a volume of water with thickness Δr and incident radiance Φ_i (everything is a function of wavelength, not written for brevity)

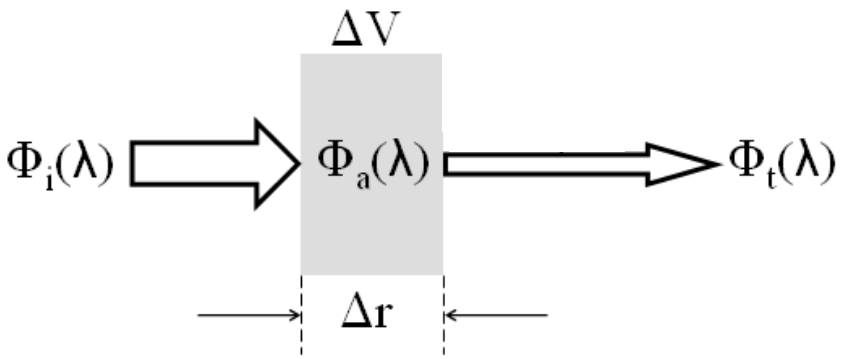
Φ_a is the radiance absorbed in the volume
$\Phi_s(\Psi)$ is the radiance scattered into angle Ψ
Φ_t is the radiance transmitted through the volume

Conservation of energy:
$\Phi_a + \Phi_s + \Phi_t = \Phi_i$

Now assume (for now) that there is no scattering so $\Phi_a = \Phi_i - \Phi_t$

Figure: Mobley et al. 2022, *The Oceanic Optics Book,* Fig. 3.1

Deriving Beer's Law



We define the absorption coefficient as the fractional radiance loss *per unit distance* through the volume.

$$a = \lim_{\Delta r \to 0} \frac{-\Delta\left(\Phi_i - \Phi_t / \Phi_i\right)}{\Delta r} = \frac{-\frac{d\Phi}{\Phi}}{dr}$$

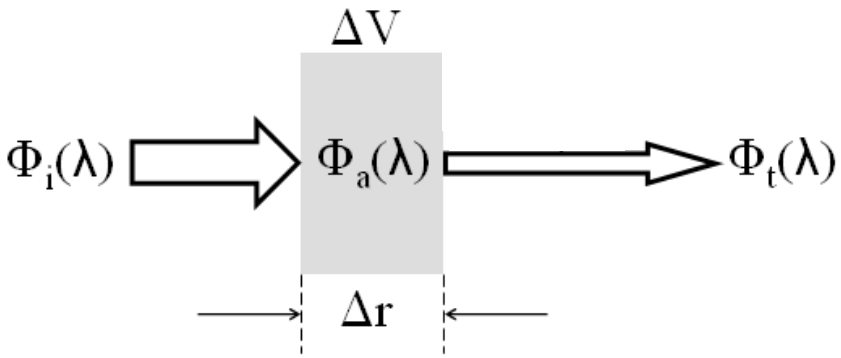
Now we can rearrange the above expression

$$a\ dr = -\frac{d\Phi}{\Phi}$$

and integrate both sides

$$\int_0^r a\ dr = \int_0^r \frac{1}{\Phi} d\Phi$$

Deriving Beer's Law



Integrating...

$$\int_0^r a\, dr = -\int_0^r \frac{1}{\Phi} d\Phi$$

$$a(r-0) = -\left(\ln\left(\Phi(r)\right) - \ln(\Phi(0))\ \right)$$

Simplify left-hand side, substitute actual Φ values in right-hand side:

$$ar = -(\ln(\Phi_t) - \ln(\Phi_i))$$

and solve for *a*

$$a = -\frac{\ln \frac{\Phi_t}{\Phi_i}}{r}$$

Units?

equivalently: $\Phi_t = \Phi_i \exp(-ar)$

Other names and symbols...

- We just derived the *absorption coefficient*

$$a = -\frac{\ln \frac{\Phi_t}{\Phi_i}}{r} \qquad [m^{-1}]$$

- Spectrophotometers (such as you will use this afternoon) often report Absorbance (A), where

$$A = -\log_{10}\left(\frac{\Phi_t}{\Phi_i}\right)$$

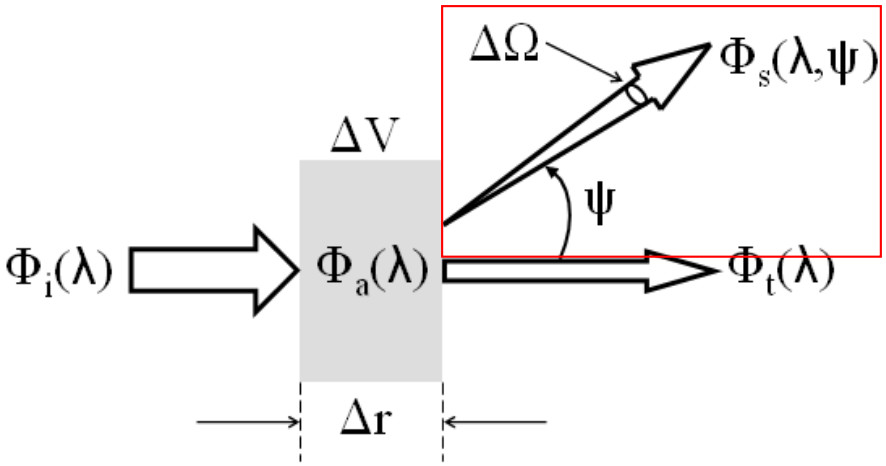
Units? Unitless!

$$a = \ln(10) * A / r$$
$$= 2.303 * A/r$$

Note that sometimes A is also called “optical density” or OD.

OK, but what about scattering? We want to measure real samples, in real instruments!

- Option 1: Remove the scatterers from the sample
- Option 2: Collect (nearly) all of the scattered light and measure a known fraction of it
- Option 3: Make well-justified assumptions about the scattered light and apply a correction



Absorption measurements when scattering is negligible

- Benchtop spectrophotometry
- Double beam and single beam configurations

1. Measure transmittance by both the sample and a reference (what should it be?)

2. Compute the sample absorbance by difference

$$A_{corr} = A_{samp} - A_{ref}$$
$$= -\log_{10}(\Phi_{t,samp}/\Phi_{t,ref})$$

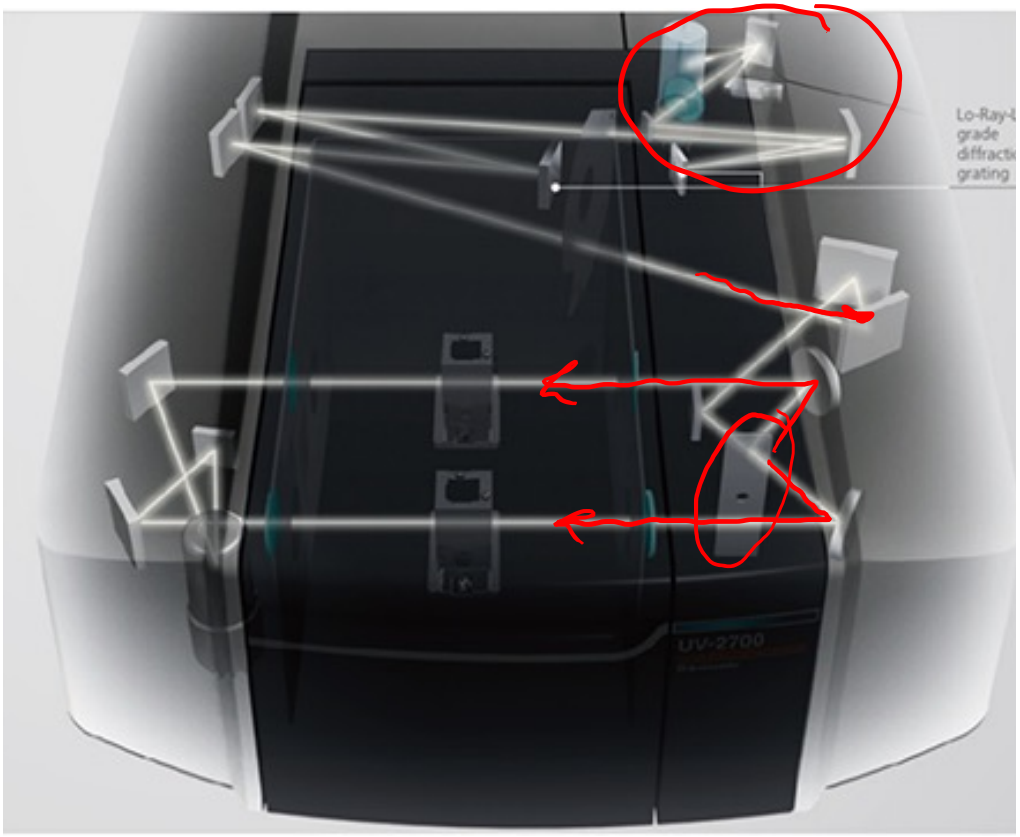


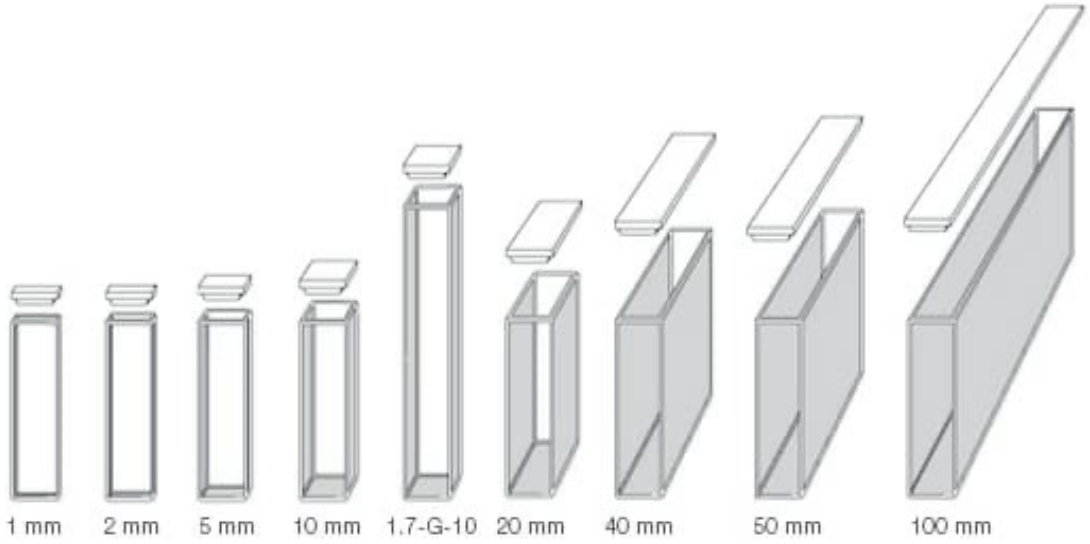
Figure: https://www.ssi.shimadzu.com/service-support/faq/uv-vis/instrument-design/25/index.html

Absorption measurements when scattering is negligible

- Benchtop spectrophotometry
- Double beam and single beam configuration
- Pathlength through sample

Recall that $A = -\log_{10}(\Phi_t/\Phi_0)$

How will the spectrophotometer's measurement of *A* change if the pathlength is large?
If it is small?



https://www.ssi.shimadzu.com/service-support/faq/uv-vis/cuvettes/1/index.html

Rule of thumb: *A* should be between ~0.1-0.4. Outside this range, the sample must be diluted or the pathlength changed.

Absorption measurements when scattering is negligible

- Benchtop spectrophotometry
- Double beam and single beam configuration
- Pathlength through sample

Liquid core waveguide (aka Liquid Waveguide capillary cell)

Measure small sample volumes (mL) in pathlengths of 0.5 m or longer

Very sensitive to bubbles, particles, careful cleaning required (eg., Floge et al. 2009, 10.4319/lom.2009.7.260)

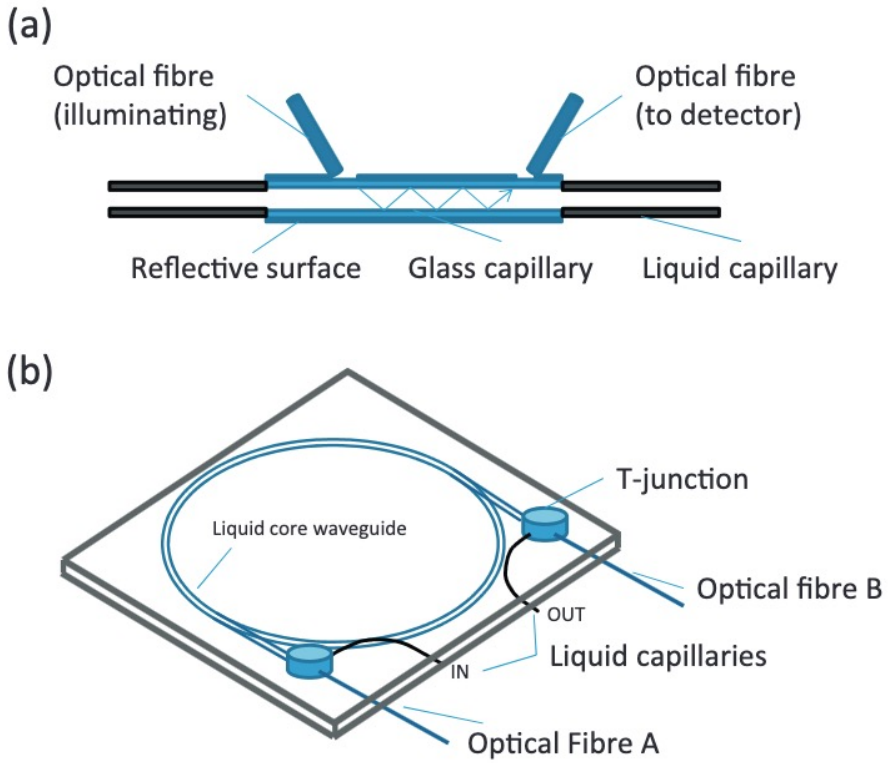
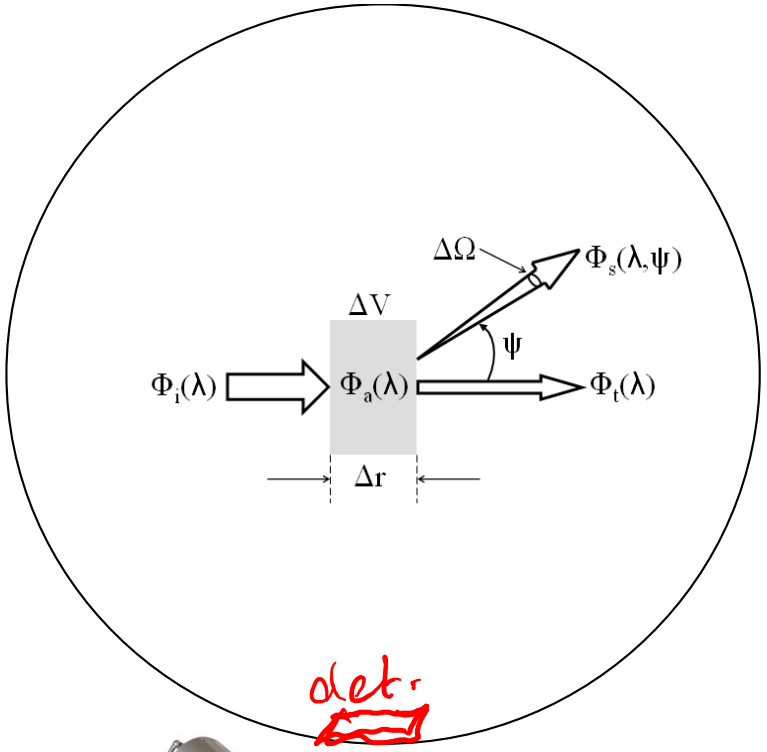


Figure: Pàscoa et al, 2012. 10.1016/j.aca.2012.05.058

Absorption measurements when scattering is not negligible (and/or a_p is of interest)

- Collect all (or nearly all) of the scattered light inside an *integrating sphere* with reflective inner surface. Measure a known fraction.
- What is the pathlength traveled by the light?
- Measure $\Phi_a = \Phi_i - (\Phi_s + \Phi_t)$



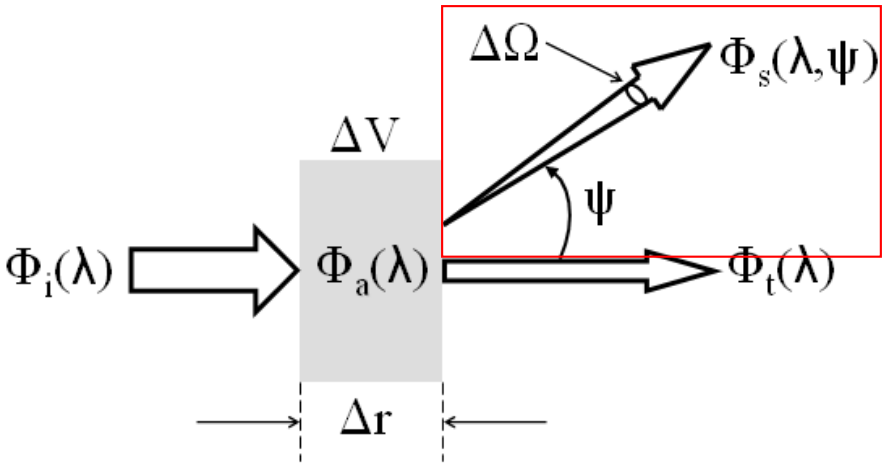
https://sunstonesci.com/product/psicam

https://www.sequoiasci.com/product/hyper-a/

https://www.trios.de/en/oscar.html

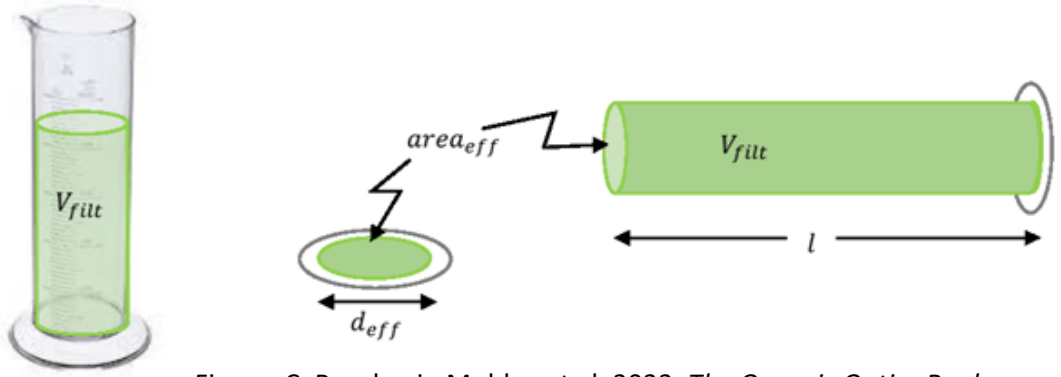
OK, but what about scattering? We want to measure real samples, in real instruments!

- Option 1: Remove the scatterers from the sample
- Option 2: Collect (nearly) all of the scattered light and measure a known fraction of it
- Option 3: Make well-justified assumptions about the scattered light and apply a correction



Filter-pad absorption measurements

- Determine the geometric pathlength from the volume filtered and the area of the filter that the sample passed through
- Put the filter over the detector port of the spectrophotometer, at the entrance/exit of an integrating sphere, or in the center of an integrating sphere, and measure the absorbance.
- Also measure and subtract the absorbance of a similarly-moistened blank filter. Collect blank scans in triplicate to estimate uncertainty.
- **Is simply subtracting the absorbance (which is mostly scattering...) of a blank filter sufficient?**



Figure, C. Roesler, in Mobley et al. 2022, *The Oceanic Optics Book*

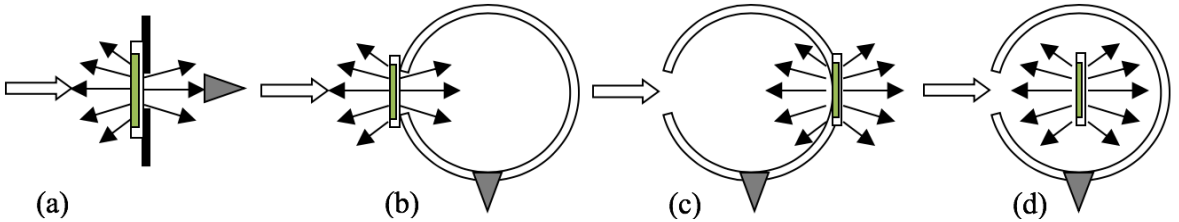


Figure 5.1. Spectrophotometric configurations for determining filter pad optical density: (a) transmittance mode (T-mode), (b and c) transmittance and reflectance mode measured with an integrating sphere with externally mounted samples (T-R-mode); (d) internally mounted sample in integrating sphere (IS-mode). Open arrow indicates incident beam, black arrows indicate beams scattered from filter, grey cone indicates detector for the generalized model.

Figure: Roesler et al., "Chapter 5: Spectrophotometric Measurements of Particulate Absorption Using Filter Pads", *in* Neeley et al., 2018. doi:10.25607/OBP-119

Filter-pad absorption measurements

Is simply subtracting the absorbance (which is mostly scattering...) of a blank filter sufficient?

- There is additional scattering off the filter fibers which causes pathlength amplification.
- Even after subtracting the absorbance of the blank, pathlength amplification still increases the probability of absorption relative to the same sample in suspension

Solution: Apply an empirical correction relating *A* on the filter pad to *A* in suspension.

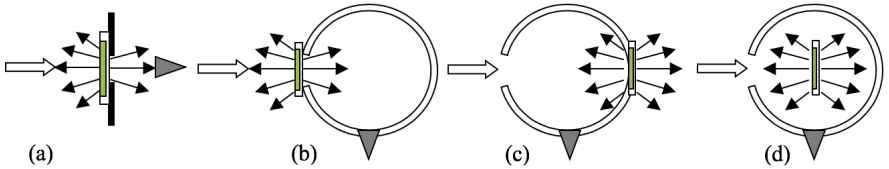
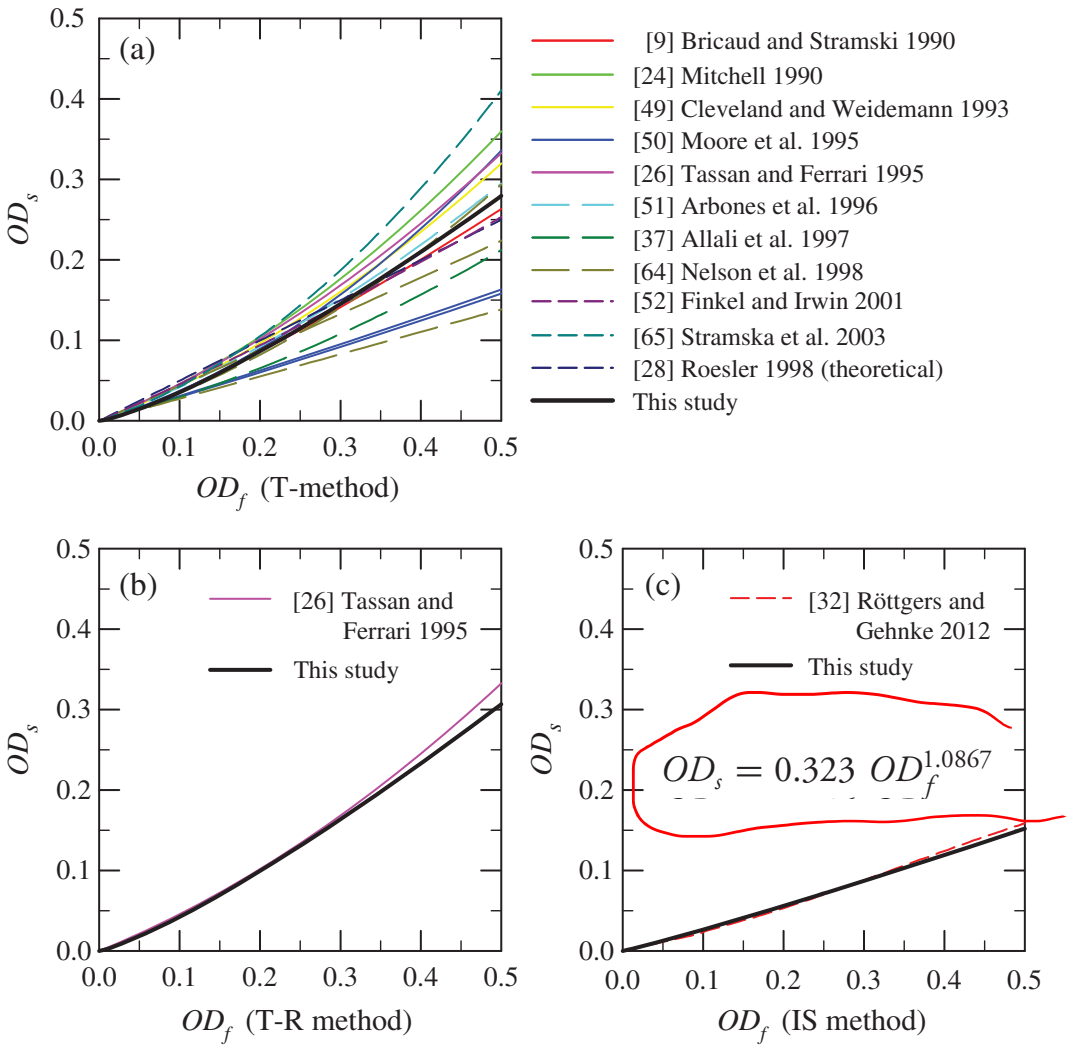


Figure: Figure: Roesler et al., "Chapter 5", *in* Neeley et al., 2018. doi:10.25607/OBP-119

Figure: Stramski et al. 2015, 10.1364/AO.54.006763



Reflecting-tube absorption & attenuation meters

- Measure absorption and beam attenuation simultaneously. Use the beam attenuation measurement to correct for undetected scattered light in the absorption measurement. Compute scattering by difference.
- Absorption measured in a cylinder with reflective interior and a diffuser in front of the detector. Only light scattered through angles > ~42° is lost.
- Attenuation measured in a cylinder with black, non-reflective walls and a detector with a narrow field of view

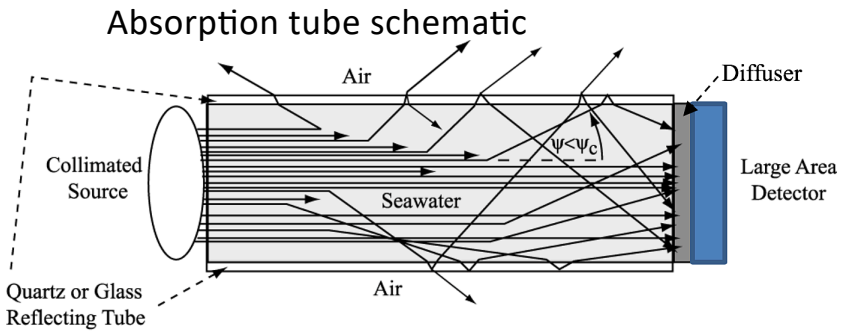
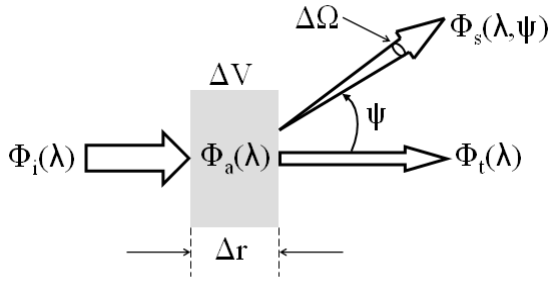
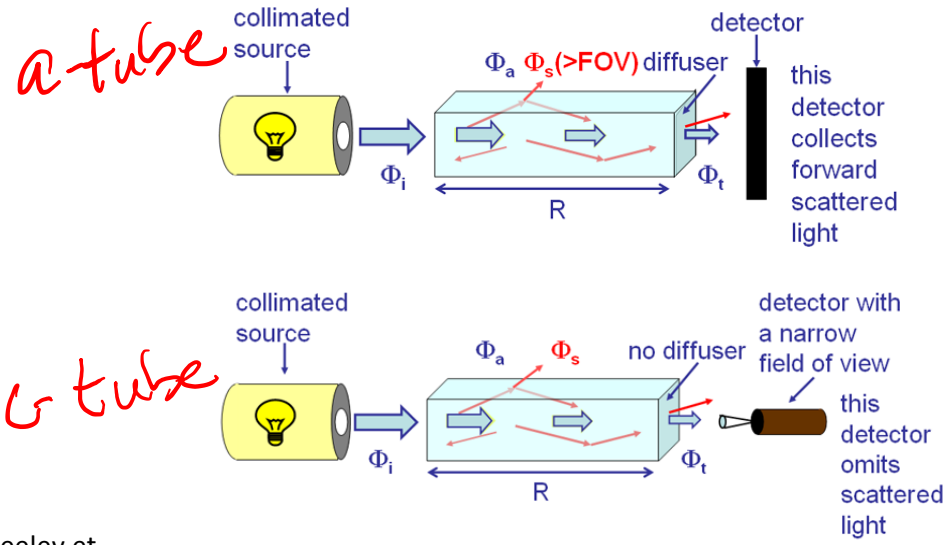


Figure: Twardowski et al., "Ch. 2: Reflective Tube Absorption Meters", *in* Neeley et al., 2018. doi:10.25607/OBP-119





Figures 3.8-3.9, Mobley et al. 2022, *The Oceanic Optics Book*

Reflecting-tube absorption & attenuation meters

b = scattering
c = beam attenuation
b = *c* – *a*

But!

Absorption is overestimated because not all the scattered light is detected in a-tube

Attenuation is underestimated because a little bit of scattered light *is* detected in c-tube

$a_m(\lambda)$, $b_m(\lambda)$, $c_m(\lambda)$ = measured spectra

Photo: ac-s datasheet, https://www.seabird.com/asset-get.download.jsa?id=54627862140

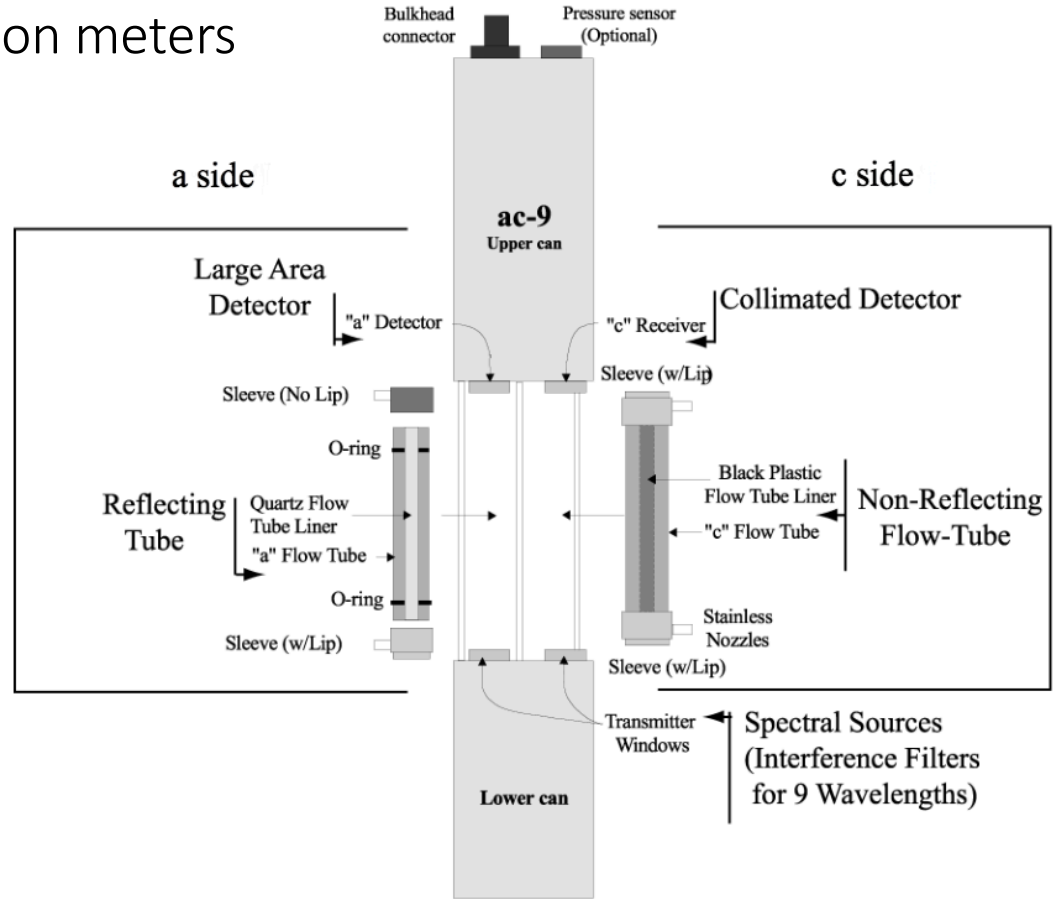


Figure 2.3. Schematic illustration of the ac-9 beam attenuation and absorption meter (courtesy of Sea-Bird Scientific).

Figure: Twardowski et al., "Ch. 2: Reflective Tube Absorption Meters", *in* Neeley et al., 2018. doi:10.25607/OBP-119

Reflecting-tube absorption & attenuation meters

- $a(\lambda)$ = true absorption spectrum (measured in suspension in an integrating sphere)
- For measured $a_m(\lambda)$, $c_m(\lambda)$:
  - temperature-salinity corrections performed
  - pure water absorption already removed

Use the calculated scattering $b_m(\lambda)$ to estimate the scattering *correction* ε (Zaneveld, 1994). Assume $a_m(\lambda_r)$ in the near infrared (NIR) is zero...

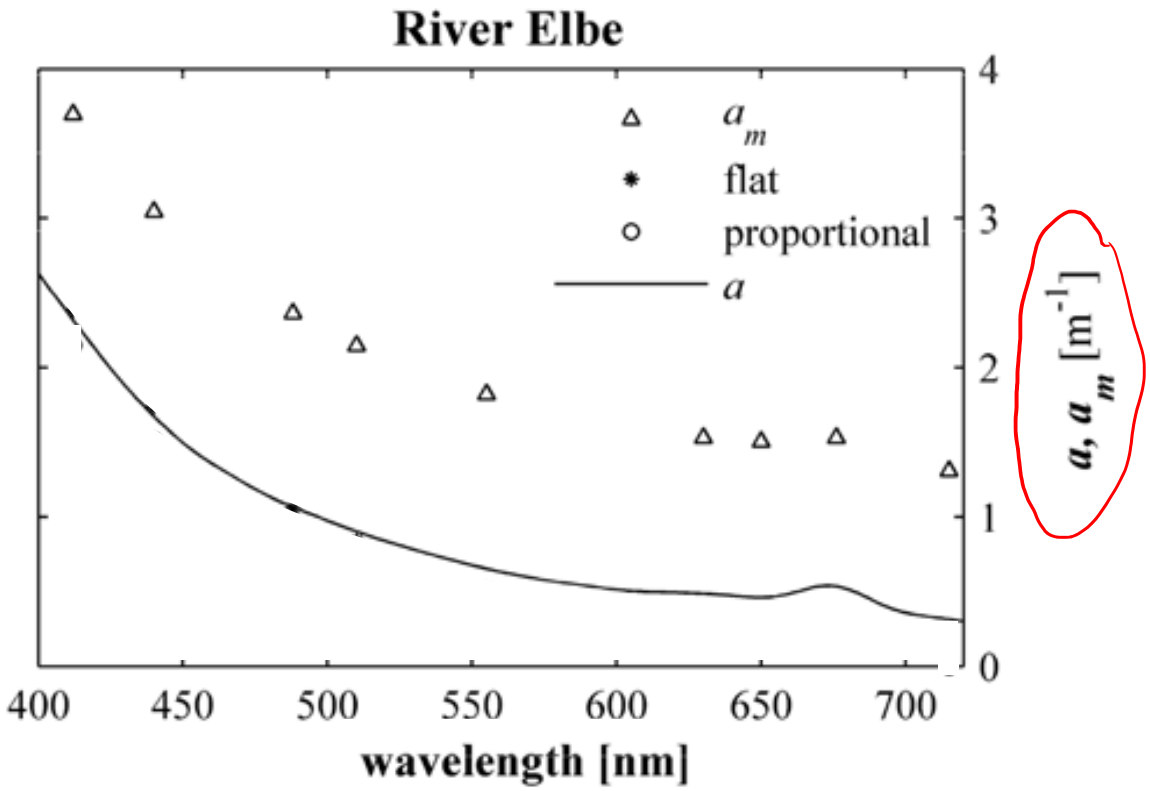


Figure: Röttgers et al., 2013. 10.1016/j.mio.2013.11.001

Reflecting-tube absorption & attenuation meters

- $a(\lambda)$ = true absorption spectrum (measured in suspension in an integrating sphere)
- For measured $a_m(\lambda)$, $c_m(\lambda)$:
  - temperature-salinity corrections performed
  - pure water absorption already removed

Use the calculated scattering $b_m(\lambda)$ to estimate the scattering *correction* ε (Zaneveld, 1994). Assume $a_m(\lambda_r)$ in the near infrared (NIR) is zero...

Option 1 "Flat": ...and that ε is the same at all wavelengths.

Option 2 "Proportional": ... or that ε is equal to a constant *proportion* of the measured scattering

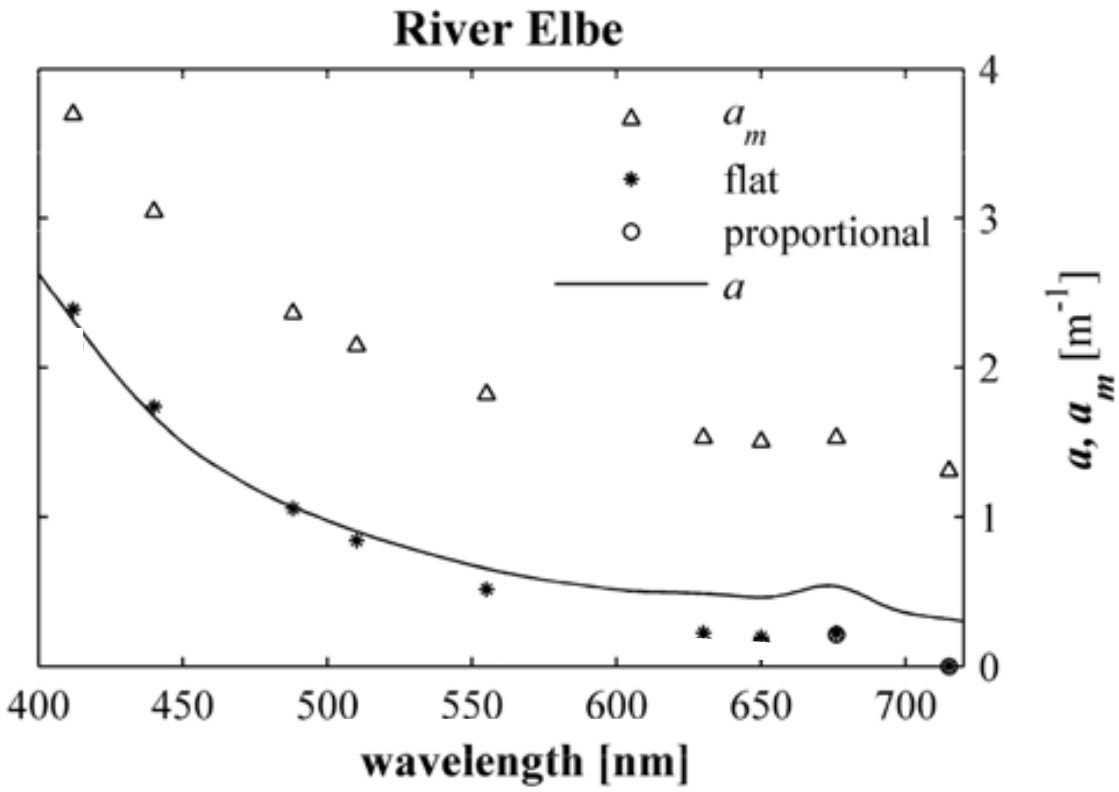


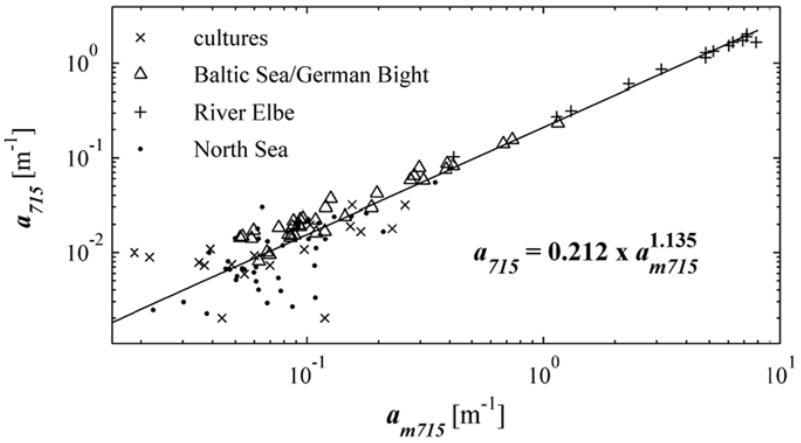
Figure: Röttgers et al., 2013. 10.1016/j.mio.2013.11.001

Reflecting-tube absorption & attenuation meters

What if you don't want to assume that $a_m(715)$ is zero?

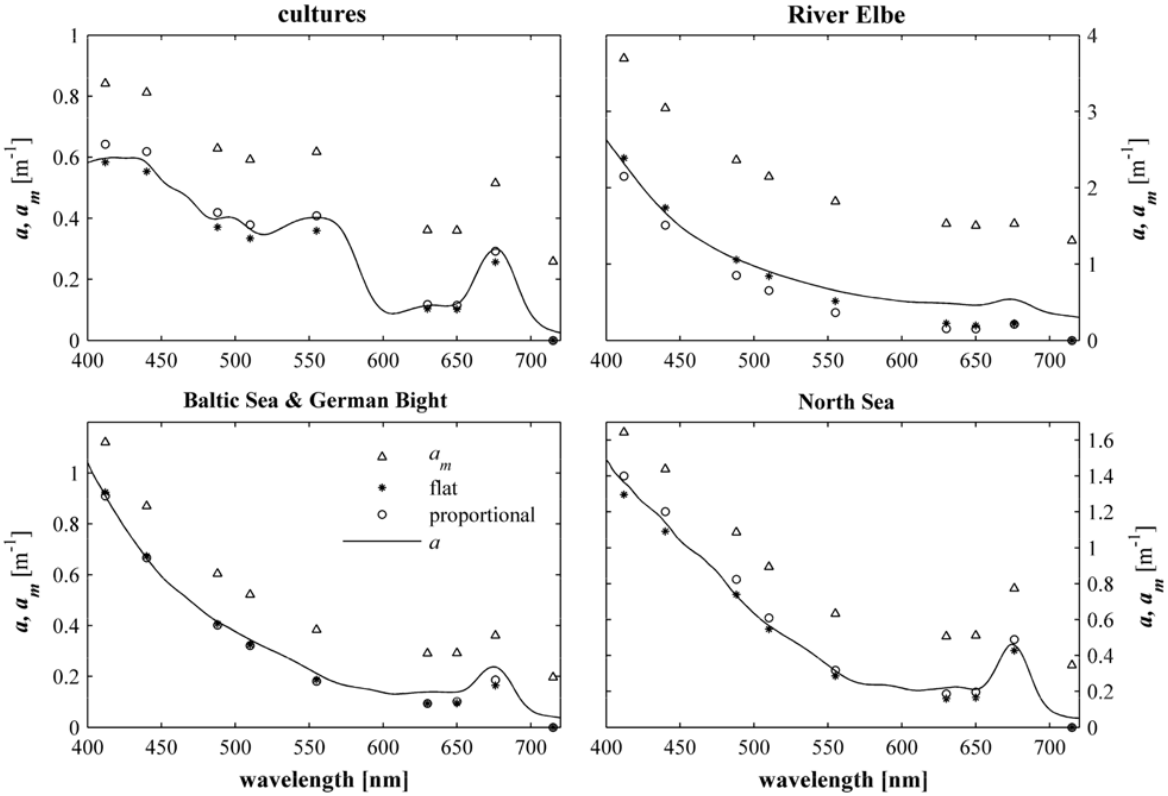
Empirical correction of Röttgers et al. 2013:

1. Compute $a(715)$ from empirical fit to measured and "true" absorption (in suspension, in an integrating sphere):



2. Correct c(λ) for underestimation due to finite detector acceptance angle (more tomorrow!)

3. *Then* do "proportional scattering correction"



Figures: Röttgers et al., 2013. 10.1016/j.mio.2013.11.001

After $a(\lambda)$ and $c(\lambda)$ have been scatter-corrected (by any method), you need to recompute $b(\lambda)$.

Closure

Kostakis et al. (2021): multi-investigator intercomparison of absorption measurements in relatively high-absorption coastal water in Florida.

Think-pair-share: Look at the terms/parameters/methods in the table and figures. Do you feel like you have the vocabulary to read Kostakis et al?

Instrument	Method	Number of sensor systems	Original spectral range (resolution)	Absorption parameter(s) directly measured	Absorption parameter derived
PSICAM	Bench top integrating sphere	1	360–728 nm (2 nm)	a_{nw}, a_{CDOM}	a_p
Turner Designs ICAM	In situ integrating cavity	2	365, 440, 488, 510, 532, 555, 590, 630, 676	a_{nw}, a_{CDOM}	a_p
WET Labs AC-s	In situ reflective tube	1	AC-s 1: 399–741 nm (mean: 4 nm) AC-s 2: 401–726 (mean: 3.7 nm)	a_{nw}	—
WET Labs AC-9	In situ reflective tube	2	412, 440, 488, 510, 532, 555, 650, 676, 715	a_{nw}	—
TriOS irradiance quartet	Gershun	1	320–900 nm (2 nm)	a_t	a_{nw}
ISFP	Bench top spectrophotometer with filter pad inside integrating sphere	2	ISFP 1: 400–750 nm ISFP 2: 300–850 nm (both 1 nm)	a_p, a_{nap}	a_{ph}
QFT-ICAM Filter pad	Bench top integrating sphere with filter pad inside cavity	1	340–844 nm (2 nm)	a_p, a_{nap}	a_{ph}
LWCC	Bench top capillary waveguide	1	240–750 nm (2 nm)	a_{CDOM}	—
Cary E3 UV–VIS spectrophotometer	Bench top dual-beam spectrophotometer with 10-cm cuvettes	1	400–750 nm (1 nm)	a_{CDOM}	—

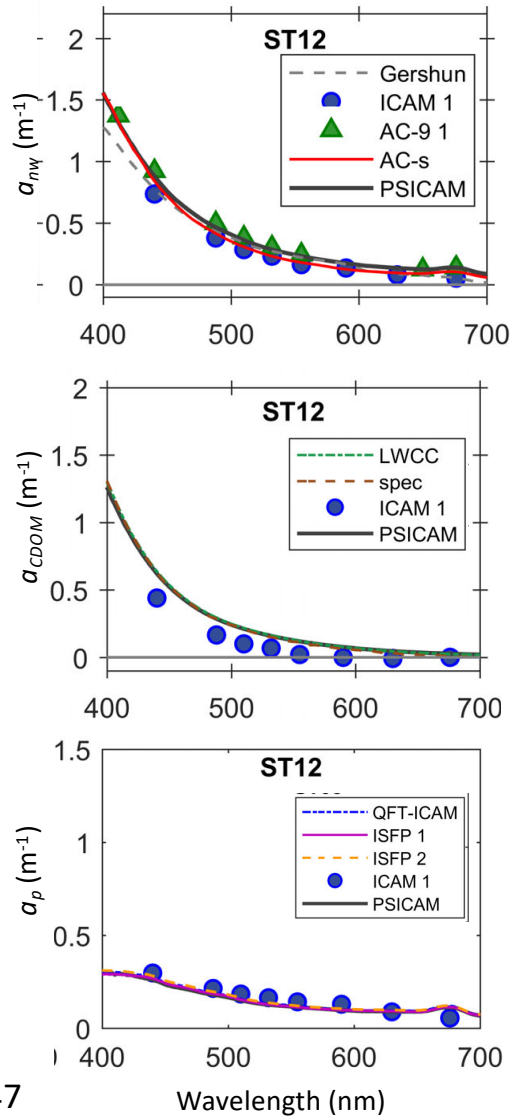


Figure and table: Kostakis et al (2021). 10.1002/lom3.10447

Absorption, part 2

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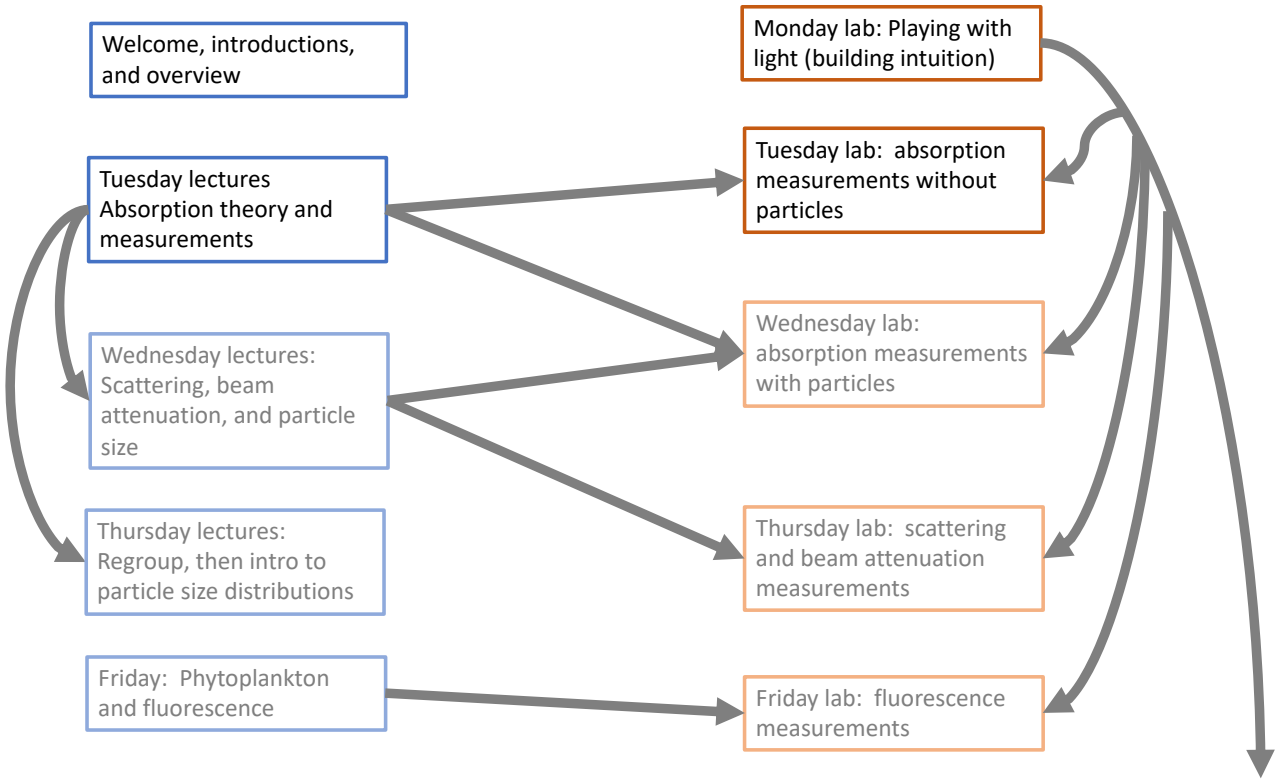
  - Realistic
- Survey of measurement techniques
- Lab overview



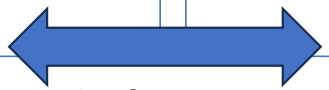
Lab today: absorption by CDOM

Group 1

- Beer's Law demonstration (simple, hands-on)
- Benchtop spectrophotometer
  - Effect of salinity and temperature
  - Effect of geometric pathlength
  - How to
    - Clean and care for cuvettes and the instrument
    - Collect absorbance measurements relative to appropriate reference solutions

Group 2

- ac-meters
  - Effect of salinity and temperature
  - Effect of geometric pathlength
  - How to
    - Clean and care for the instrument
    - Acquire pure-water readings
    - Correct for temperature and salinity effects
  - First steps of data analysis



Switch after 90 minutes

Lab today: absorption by CDOM

Broad questions to answer as a group, presented at the start of the day tomorrow:

1. *How does the absorption spectrum of purified water vary with temperature?*
2. *How does the absorption spectrum of purified water vary with added salt (salinity)?*
3. *How does the dye concentration (in the Beer's Law demonstration) affect the absorbance of a solution?*
4. *How does the geometric pathlength impact the measured absorbance and the derived absorption coefficient?*
5. *What factors influence the CDOM spectral slope (e.g. instrument, wavelength range, sample type)?*

You will need to combine measurements from all groups this afternoon to answer the questions!