Introduction to Colorimeters:

Theory, Products, and Application

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Topics

- History and science of colorimeters
- Taking a measurement
- Troubleshooting and alternative techniques
- Hanna photometers
- Identifying colorimeter customers
- Applications

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- **History and science of colorimeters**
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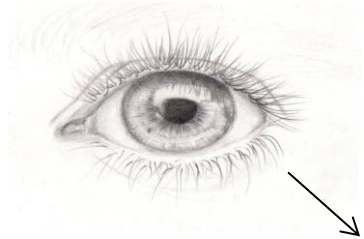
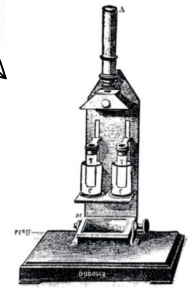
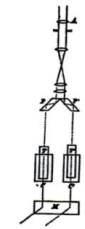
Timeline







1300 → First chemical litmus is discovered

1856 → Julius Nessler proposes a method of determining ammonia concentration

1870 → Deboscq color comparator

1919 → Null type method photoelectric colorimeter

1928 → Direct reading colorimeter

1954 → Bausch and Lomb - Spec 20

1960 → Widespread use of colorimetry

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History

- Colorimetry began with the use of chemical test kits
  - A reagent reacts with the sample to form a visible compound that is compared to a key
  - The concentration of a compound in the sample is directly related to the intensity of the color produced

- Color comparators evolved to improve accuracy

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Chemical Test Kits

Advantages

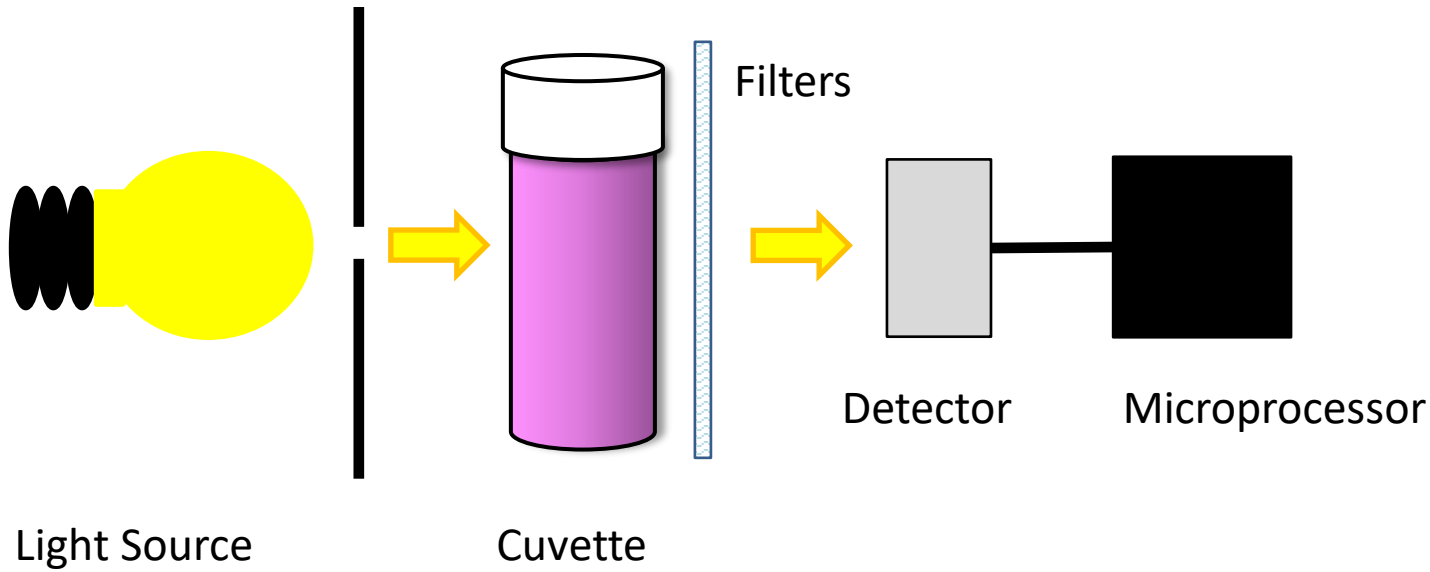
- Inexpensive
- Little skill required

Disadvantages

- Subjective
  - Not everyone sees color the same way
  - Color blind users
- Low resolution
  - Only a few points of resolution (i.e. chlorine copper test kit – 0.5 mg/L resolution)

Technological Advancements

- Instruments with light sensors (photoelectric cell) improve the measurement process
- Using a meter to determine light intensity eliminates the subjectivity of the human eye



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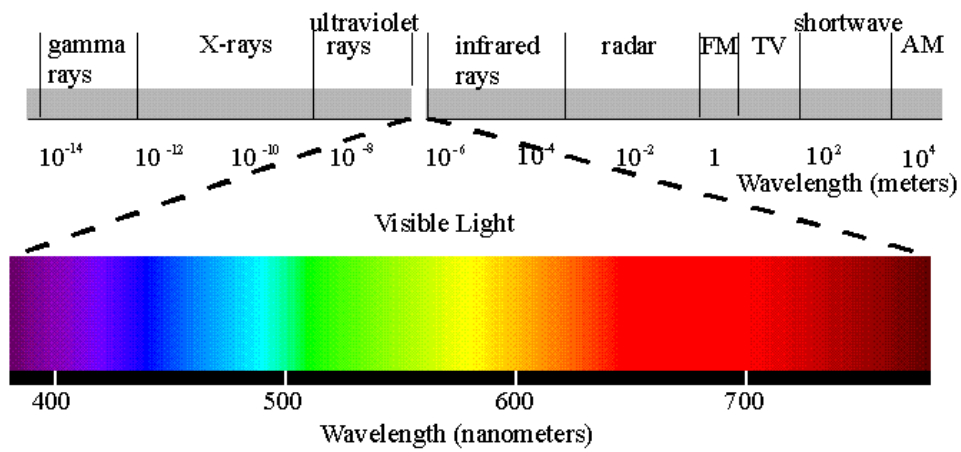
Visible Light Spectrum

- Visible light refers to the electromagnetic wavelengths that the human eye can see
- White light is made up of seven colors (violet, indigo, blue, green, yellow, orange, and red)
- Each color represents a wavelength of light between about 390 and 750 nanometers (nm)



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Absorbance

- Substances have the ability to absorb and reflect light
  - White material reflects all colors (i.e. snow)
  - Black material absorbs all colors (i.e. charcoal)
- A substance of a particular color will absorb its complementary color
  - Complementary colors are opposite on the color wheel
  - A red object absorbs green light and reflects red light

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Absorbance

Wavelength (nm)	Color Observed	Color Absorbed
400	Violet	Yellow-Green
435	Blue	Yellow
495	Green	Purple
560	Yellow	Blue
650	Orange	Greenish Blue
800	Red	Bluish Green

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Absorbance

Absorbance of light by a complementary color

- Green light is absorbed by red solution

Passage of light by the same color

- Red light is not absorbed by a red solution

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Absorbance vs. Transmittance

Absorbance

$$A = \log_{10} (I_o / I)$$

- The amount of light absorbed by a solution

Transmittance

$$T = I / I_o$$

- The percent of light transmitted through a solution

I = light intensity after passing through a reacted sample

I_o = light intensity after passing through an unreacted sample

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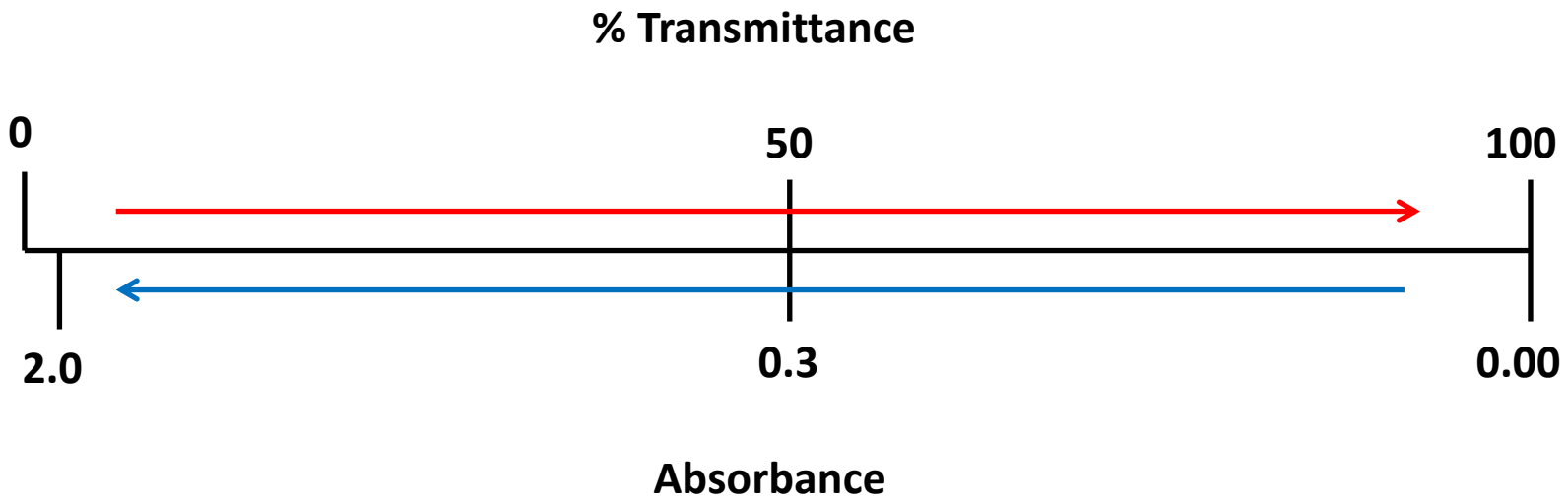
Absorbance vs. Transmittance



- In general, as one increases, the other decreases
- As path length increases, % transmittance *decreases* and absorbance *increases*

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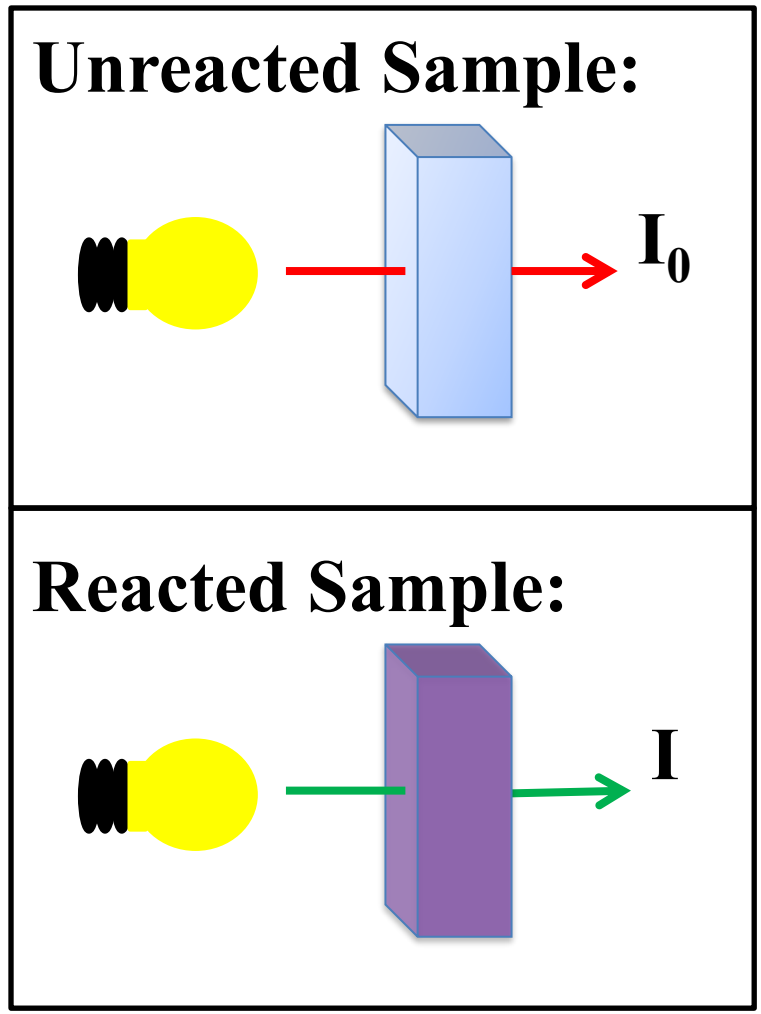
Photometry

- Photometry is the measurement of light
- As light passes through a solution, some of it is absorbed
- The difference in intensity of light before ($\mathbf{I_o}$) and after (**I**) a reagent is added is used to determine the concentration of the specific substance in the sample



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Beer-Lambert Law

- $A=\epsilon_{\lambda}(C)(L)$
  - ϵ_{λ} is the molar extinction coefficient
  - **C** is the molar concentration of the solution
  - **L** is the optical path length
- **Absorbance** depends on the **concentration** of the absorbing compound that is in the path of light going through the cuvette

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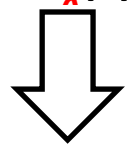
Molar Extinction Coefficient

$$A=\epsilon_{\lambda}(c)(L)$$



$$\epsilon_{\lambda} = A /(c)(L)$$

- ϵ_{λ} represents the *absorption efficiency of a substance*
- It is always constant for a particular substance at a specific wavelength (λ)
- ϵ_{λ} is a *measure of the amount of light absorbed per unit concentration*

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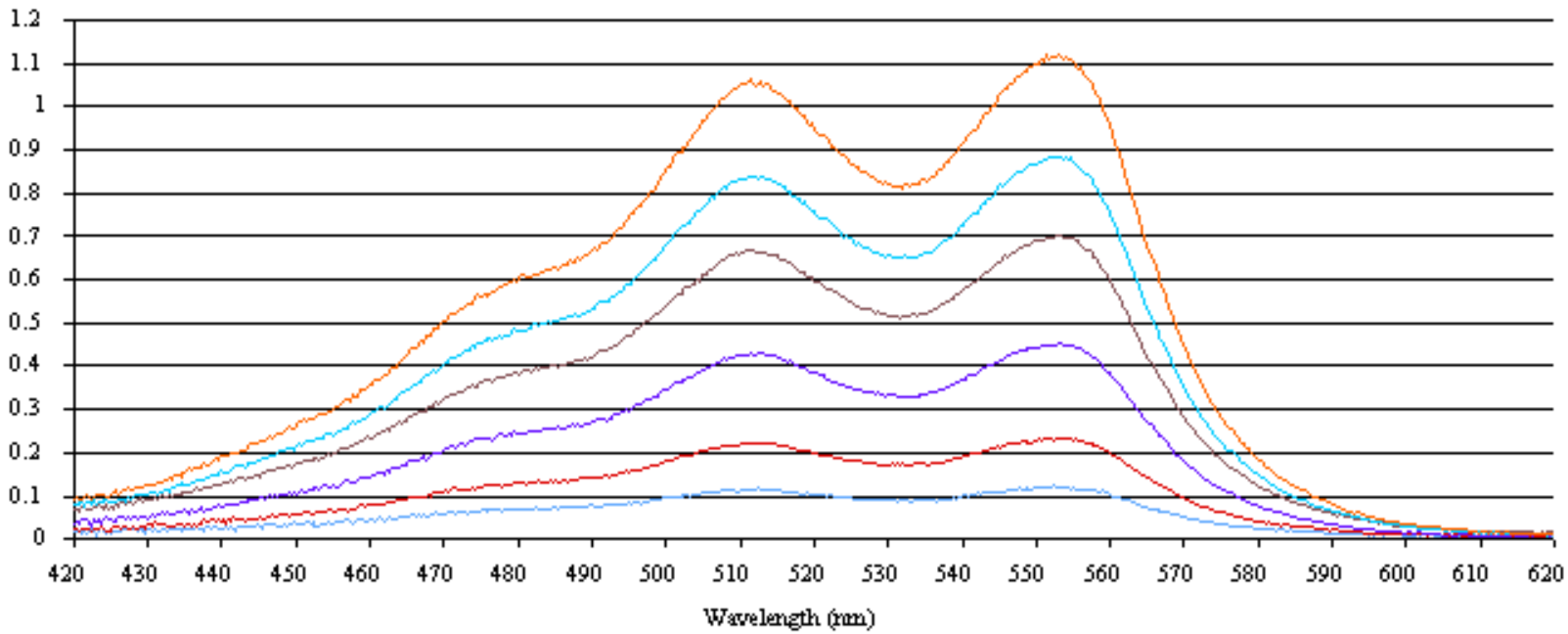
Molar Extinction Coefficient



Typical Absorption Spectrum for Chlorine Reaction with DPD

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Molar Extinction Coefficient

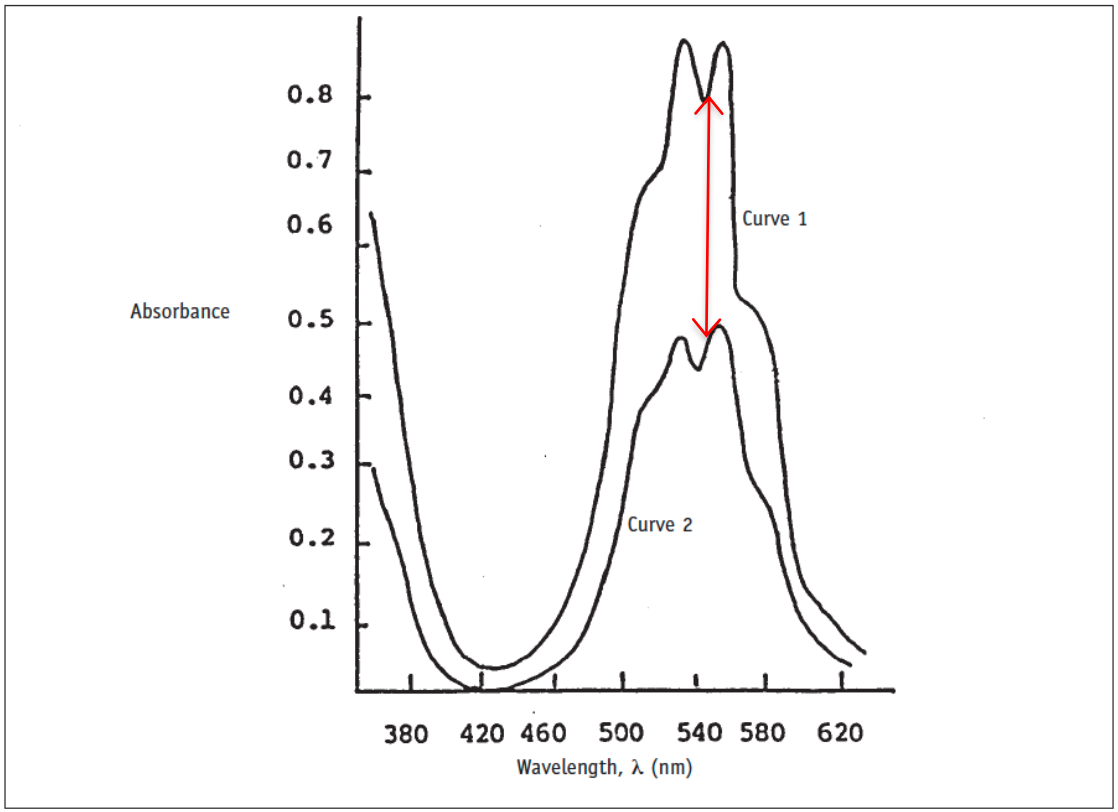

FIGURE The absorption spectrum of solutions of potassium permanganate ($KMnO_4$) at two different concentrations. The solution for curve 1 has a *higher* concentration than that for curve 2.

- Also known as **molar absorptivity**- efficiency of a molecule for the adsorption of light
- Generally select wavelength where the maximum absorbance occurs
- Maximum distance between the two samples of different concentrations. For the plot on the left this occurs at 525 nm.
- Using steep part of a curve will result in large errors for slight fluctuations

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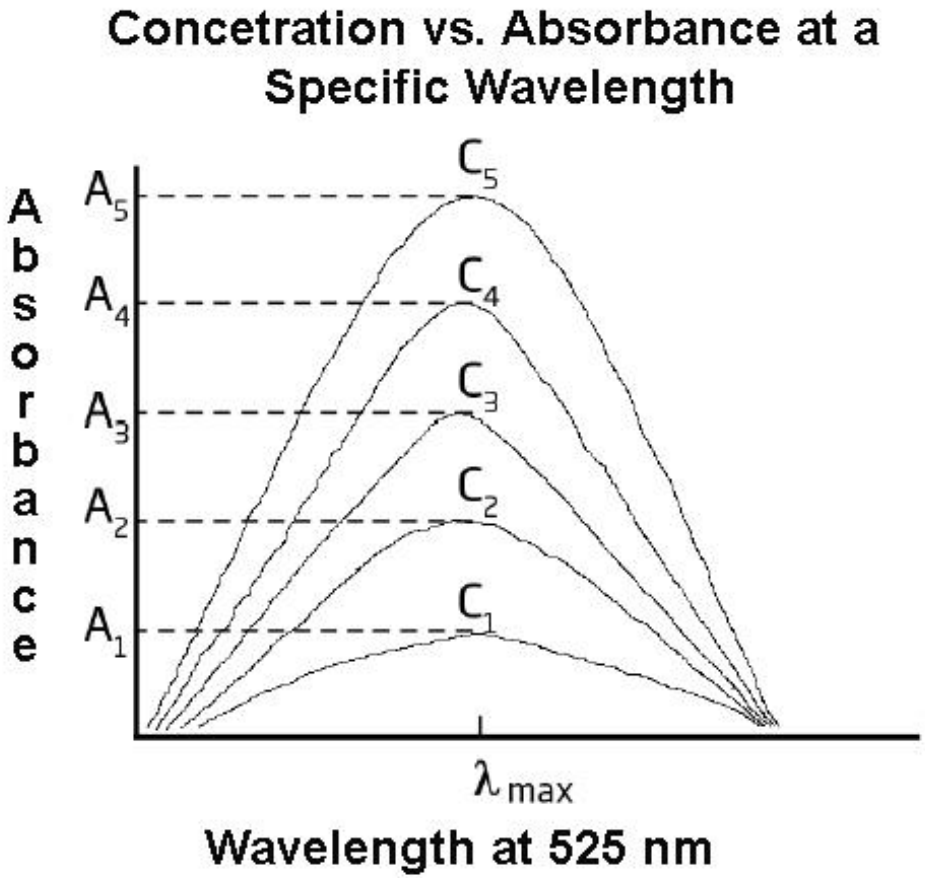
Molar Extinction Coefficient



- Absorbance related to concentration at a specific wavelength
- More molecules present = more light adsorbed
- Plot to the left shows maximum absorbance at 525 nm for all concentrations

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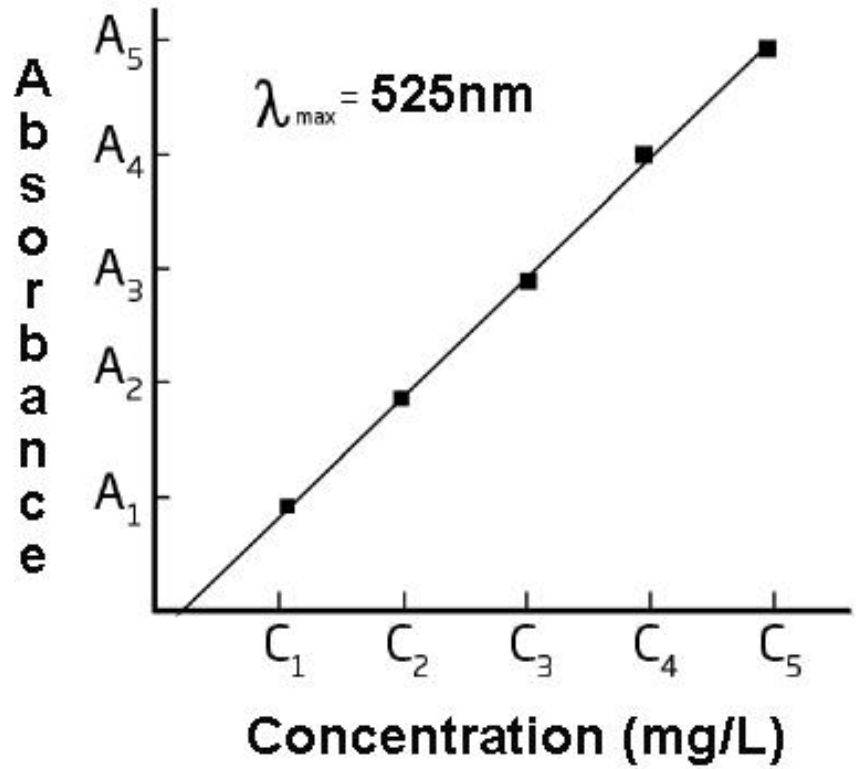
Molar Extinction Coefficient

Consider the formula for a line: **y=mx+b**

- **y** is absorbance
- **x** is concentration multiplied by the path length
- **b** is zeroed out from the first reading
- **m** (slope) is the molar extinction coefficient



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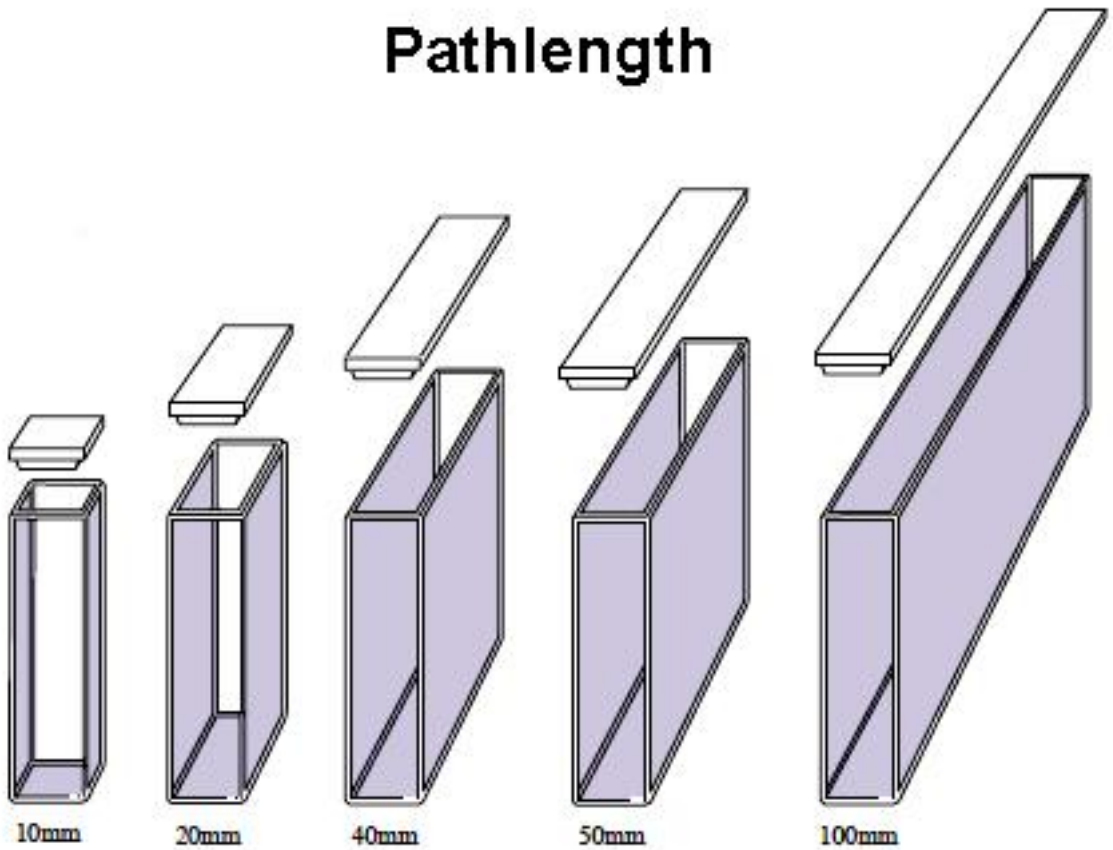
Path Length



$$A=\epsilon_{\lambda}(c)(L)$$

- Path length (L) is the distance the light travels
- Longer path length results in an increased absorbance
- Increased accuracy for samples with low absorbance

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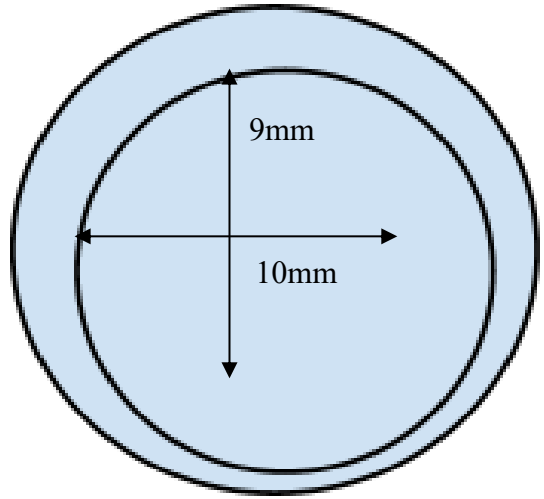
Path Length



$$A=\epsilon_{\lambda}(c)(L)$$

- Indexing of round sample cells (cuvettes)
  - Cuvettes are NOT uniformly round
  - Differences in the uniformity will change the path length
  - ALWAYS index the cuvette to make sure that the path length is the same

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Using Beer-Lambert

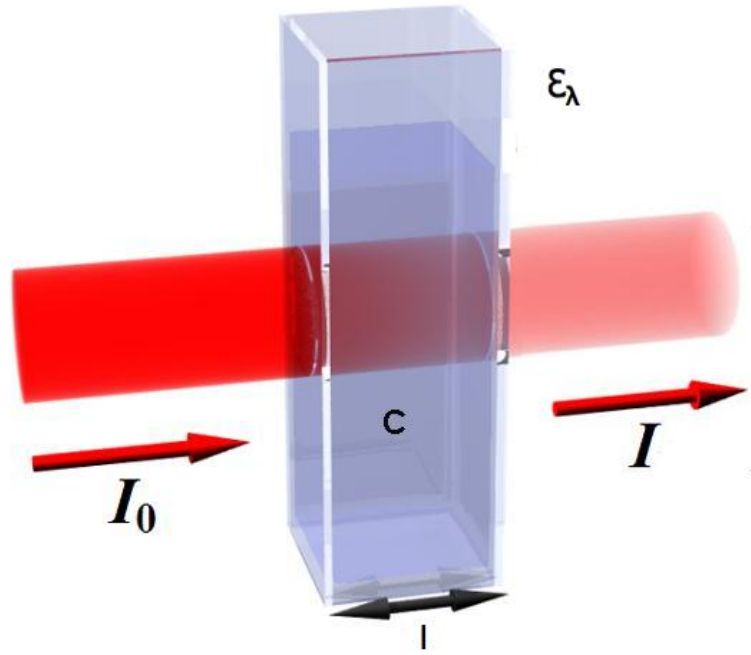
$$A = \varepsilon_{\lambda} \cdot C \cdot I$$

A = absorbance which is the difference between I_0 and I

ε_{λ} = is the molar extinction coefficient $^{[L/(mol \cdot cm)]}$ at a specific wavelength and temperature

C = concentration $^{(mol/liter)}$

I = path length $^{(cm)}$



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Light Options

- Tungsten Bulbs
  - Used in portable and bench top meters
  - Produces “white” light (includes all of the colors of light)

- LEDs
  - Used in pocket colorimeters
  - Emits a specific wavelength of light
  - Does not require a filter

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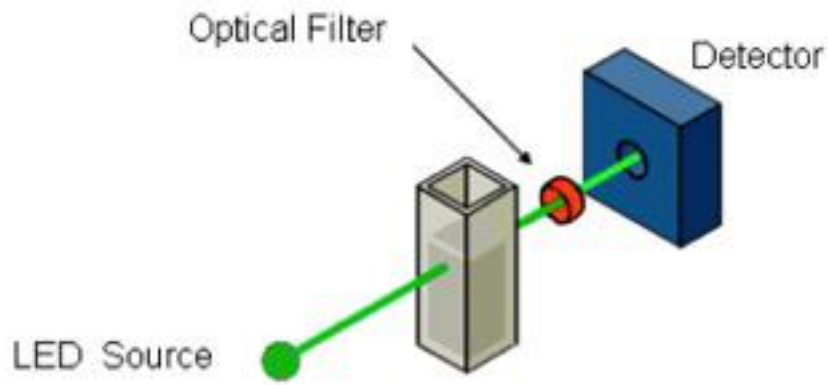
Light Options

- Pocket vs. Portable Colorimeters
  - Both use LEDs
  - Portable use a narrow band interference filter



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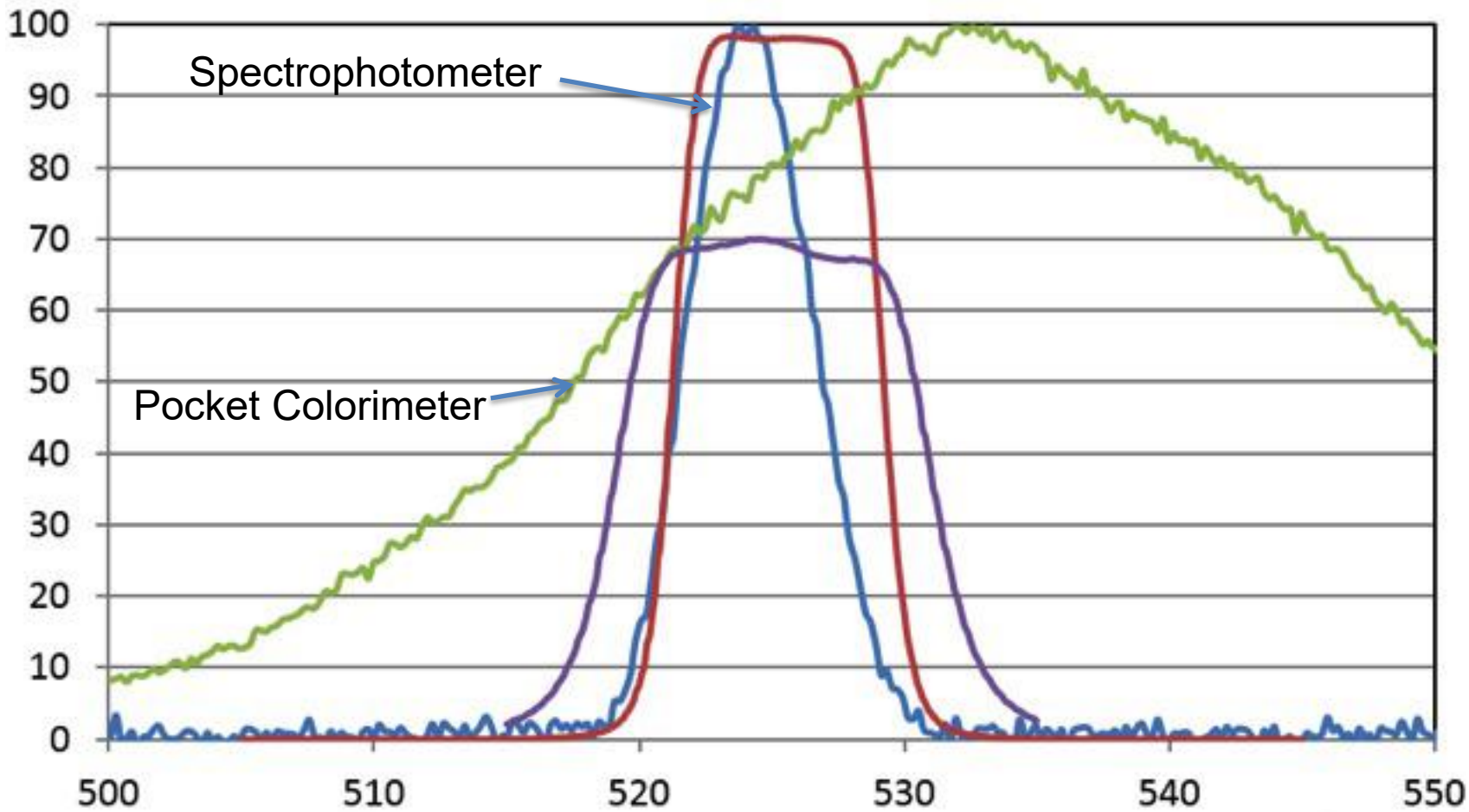
Light Options



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Wavelengths

- Milwaukee photometers can measure up to 10 different parameters using twos wavelengths of light

Wavelength	LED Color	Sample color	Example
525 nm	Green	Red	Chlorine
466 nm	Blue	Yellow	Ammonia

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How to Perform a Test

- Collect the sample
- Prepare the sample
- Place the sample in the photometer
- Zero (blank) the sample
- Add reagent (chemistry)
- Place the reacted sample in the photometer
- Read the value at appropriate timed interval

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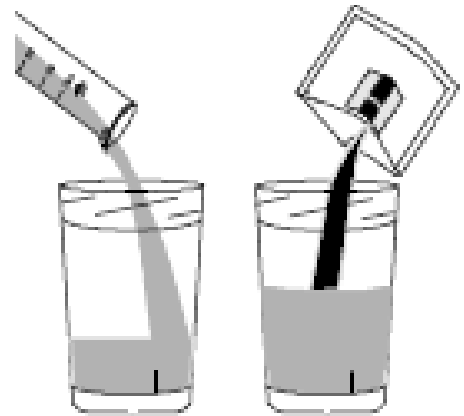
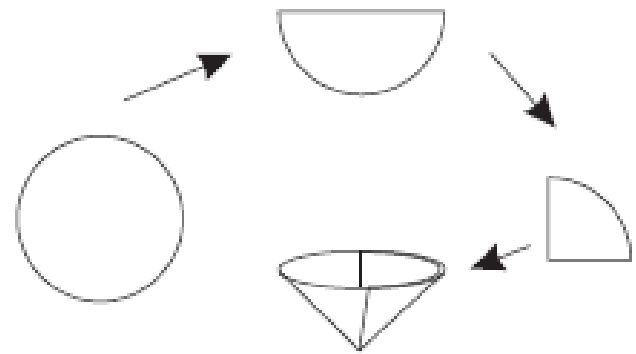
Sample Preparation:
Turbidity and Color Removal



- Turbidity scatters light → dispersion
- Excess color (sometimes is present in water) → too much absorption of the appropriate wavelength

BOTH CAUSE MEASUREMENT ERRORS

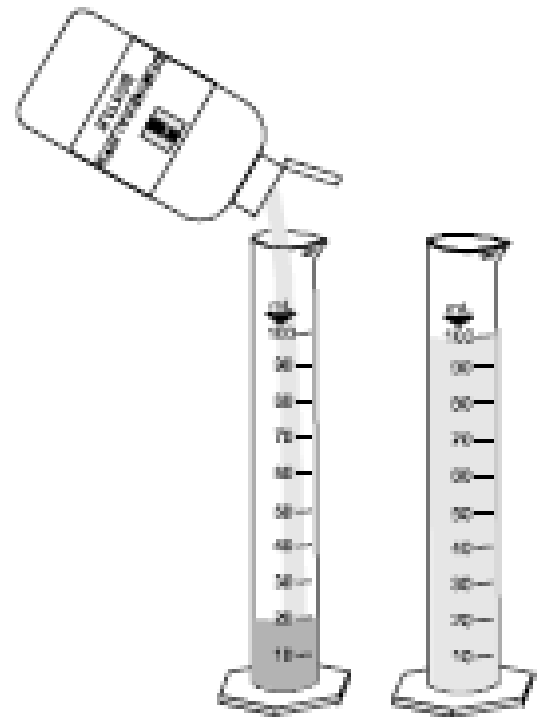


- If there is excess color or turbidity it can be removed
  - Mix the sample with a packet of active carbon*
  - Let stand for 5 minutes
  - Prepare a filter cone and filter the solution

*Active carbon can sometimes remove the compounds that are of interest (i.e. chlorine).

Sample Preparation: *Dilution*

Some samples contain concentrations which are above our testable range.



Decreasing a solutions concentration is called *dilution*.

Step 1: Take a known volume of sample to be tested.

Step 2: Add a known volume of deionized water.

Step 3: Test sample dilution and multiply by factor.

For example:

If you add 9 ml of deionized water to a 1 ml sample that has 15 mg/L chlorine, it will result in a 1.5 mg/L solution.

Since a 1:10 dilution was performed , the reading would then need to be multiplied by 10.

Zero (Blank) Measurement

It is important to establish a zero reading before adding reagent to the sample

1. Place an unreacted sample into the colorimeter and take an initial reading (I_o)
   - This compensates for any color present
   - The reagent for a chlorine test turns the sample pink – this would account for any pink already present in the sample

2. Ensure the door is closed tightly and securely to prevent the introduction of stray light

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Add Reagent (Chemistry)

- Produces a color in the sample
- Forms a new compound that can be seen and detected
  - Some of the light passing through the solution is absorbed by the color in the solution
  - The rest of the light that is not absorbed is then measured
- Reaction time
  - A preset reaction time is required before measurement
  - Too much time → side reactions
  - Built-in timer

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Troubleshooting

- Beer-Lambert equation

$$A = \log_{10}(I_o/I) = \varepsilon_\lambda(C)(L) \qquad C = \log_{10}(I/I_o)/\varepsilon\lambda\,(L)$$

- Light
  - Check to make sure the light is working
  - Eliminate stray light (removes I_o as the problem)
  - Cuvette is indexed properly (removes L as the problem)
- Sample
  - Ensure the sample has been prepared properly and that there is no chemical interference (removes I as the problem)
- That leaves → ε_λ

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Interferences

- Specific **ions** impact certain tests
- **pH** can affect reagent chemistry:
  - Some reagents will only form a color within a range or below a set pH point
  - Groundwater tends to be more alkaline than surface water
  - Chlorine tests for groundwater may require reagents high in alkalinity
- Common interferences are listed in the portable manuals

Example: Chlorine Interferences

- Positive error
  - Bromine
  - Chlorine Dioxide
  - Iodine
  - Oxidized Manganese and Chromium
  - Ozone
- Alkalinity above 250 mg/L $CaCO_3$ or acidity above 150 mg/L $CaCO_3$ will not reliably develop the full amount of color or it may rapidly fade.
- To resolve this, neutralize the sample with diluted HCl or NaOH.
- In case of water with hardness greater than 500mg/L $CaCO_3$, shake the sample for approximately 2' after adding the powder reagent.

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Chemistry Issues

- Always ensure that the correct reagent is being used
  - Even high and low range measurements can have vastly different reagents or measurements

- The quality of reagents can break down
  - The expiration date is printed on the front of its packet
  - If the reagent breaks down, the user will experience measurement errors

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Alternative Techniques

1. ISEs
   - Not available for all solution types
   - Advanced technology
   - Costly
2. Titration
   - Costly
   - Time-intensive
   - Requires trained personnel

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The Portable PRO Family

- Designed for field work
  - Most test individual parameters
  - Some test a few parameters specific to an application
- Features
  - BEPS (Battery Error Prevention System)
  - Locking cap mechanism for proper alignment (indexing) each time

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Bridging the Gap: Checker Series

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Milwaukee Pocket Colorimeters

- Simple-to-use colorimeter
- Similar cost as a chemical test kit
- Digital read out for accurate res
- Small and portable
- Single parameter testers includi
  - Ammonia
  - Chlorine
  - Phosphate

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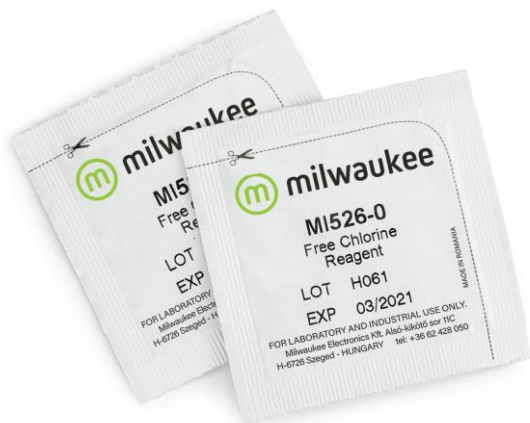
Reagents

- Spare reagents are sold separately
- The reagent is the required chemical that reacts with the sample to produce color



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Reagent Part Numbers

- A user can choose the right reagent part number by choosing “-25” or “-01” (25 and 100 tests, respectively)
- “-25” is used for Pocket Colorimeters
- Chlorine testing has both powder and liquid options

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Identifying A Customer

- When the word concentration is mentioned, think colorimeter.

Concentration → Colorimeter

- Customers currently using chemical test kits:
  - Are they aware of colorimeters?
  - What is their level of technical expertise?
  - What is the customer's concern about colorimeters?

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Applications

- Aquaculture
- Boilers/cooling towers
- Disinfection
- Education
- Environmental testing
- Honey color (Pfund)
- Maple syrup quality
- Pulp/paper Mills
- Pools/spas
- Wastewater
- Water quality
- Wine industry

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