# Lesson 2:
# All About Sunscreens

# Teacher Materials

**Contents**

# All About Sunscreens: Teacher Lesson Plan

## Orientation

This lesson introduces students to the difference between organic and inorganic sunscreen ingredients and the difference between traditional inorganic ingredients and their nanoversions. These differences include their chemical and bonding structure as well as their effectiveness in blocking UV light from reaching the skin and their appearance.

- The All About Sunscreens PowerPoint takes students through the history of why sunscreens were first developed, their current rating system for UVB blocking ability (SPF) and the need to also consider UVA blocking ability. The slides then explore the different structure and blocking mechanisms of organic and inorganic sunscreen ingredients. Finally the slides discuss what gives inorganic sunscreens their "white" or clear appearance and how the nano versions remedy this situation. There is an optional demonstration of absorption of UV light by chemicals in printed money (as an anti-counterfeiting measure) embedded in the PowerPoint presentation that you can do with your class.
- The Sunscreen Ingredients Activity gives students the opportunity to become familiar with the different ingredients used in sunscreens firsthand. This experience along with the Summary of FDA Approved Sunscreen Ingredients Handout is aimed at making students think to look at the ingredients on the label the next time they go shopping for a sunscreen.
- The Reflecting on the Guiding Questions Worksheet asks students to connect their learning from the activities in the lesson to the overall driving questions of the unit.

## Essential Questions (EQ)

What essential questions will guide this unit and focus teaching and learning?

1. What are the most important factors to consider in choosing a sunscreen?
2. How do you know if a sunscreen has "nano" ingredients?
3. How do "nano" sunscreen ingredients differ from most other ingredients currently used in sunscreens?

## Enduring Understandings (EU)

Students will understand:

*(Numbers correspond to learning goals overview document)*

2. Why particle size can affect the optical properties of a material.
3. That there may be health issues for nanosized particles that are undetermined at this time.

4. That it is possible to engineer useful materials with an incomplete understanding of their properties.
5. There are often multiple valid theoretical explanations for experimental data; to find out which one works best, additional experiments are required.
6. How to apply their scientific knowledge to be an informed consumer of chemical products.

## Key Knowledge and Skills (KKS)

Students will be able to:

*(Numbers correspond to learning goals overview document)*

1. Describe the mechanisms of absorption and scattering by which light interacts with matter.
2. Describe how particle size, concentration and thickness of application affect how particles in a suspension scatter light.
3. Explain how the phenomenon of seeing things in the world is a human visual response depending on how light interacts with objects.
4. Evaluate the relative advantages (strong blockers, UVA protection) and disadvantages (possible carcinogenic effects, not fully researched) of using nanoparticulate sunscreens.

## All About Sunscreens Timeline

| Day | Activity | Time | Materials |
|---|---|---|---|
| Day 1<br>(50 min) | Show All About Sunscreen PowerPoint Slides, using the embedded question slides and teacher's notes to start class discussion. (Embedded graph interpretation activity with student handout)<br>Perform Demonstration associated with PowerPoint Presentation (optional) | 50 min | All About Sunscreen PowerPoint Slides & Teacher Notes<br>Computer and projector<br>Optional Demonstration Materials: UV light, different kinds of paper currency.<br>Copies of Light Reflection by Three Sunscreens: Student Handout<br>Light Reflection by Three Sunscreens: Teacher Answer Key |
| | *Homework*: Read Sunscreen Ingredients Activity: Student Instructions & Worksheet | *20 min* | Copies of Sunscreen Ingredients Activity: Student Instructions & Worksheet |
| Day 2<br>(35 min) | Have students work in pairs to complete the data collection and fill in the chart in the Sunscreen Ingredients Activity: Student Instructions & Worksheet. Then have them continue to work in pairs to answer the discussion questions in the worksheet. | 10 min | Different kinds of empty sunscreen bottles as listed in the Sunscreen Ingredients Activity: Teacher Instructions & Answer Key |
| | Bring the class together as a whole to discuss questions 6-8. At the conclusion of the activity hand out and discuss the summary of FDA approved sunscreens. | 10 min | Summary of FDA Approved Sunscreen Ingredients: Student Handout |
| | Have students work individually or in small groups to fill out the Reflecting on the Guiding Questions: Student Worksheet. | 5 min | Copies of Reflecting on the Guiding Questions: Student Worksheet |
| | Bring the class together to have students share their reflections with the class.<br>This is also a good opportunity for you to address any misconceptions or incorrect assumptions from students that you have identified in the unit up till now. | 10 min | Reflecting on the Guiding Questions: Teacher Instructions & Answer Key |

**Name**_______________________________ **Date**________________________ **Period** ______

# Sunscreen Ingredients Activity: Teacher Instructions & Answer Key

This activity allows students to become familiar with the different ingredients used in sunscreens after learning about how different sunscreen ingredients work. After this activity you may want to give students the handout "Summary of FDA Approved Sunscreen Ingredients" to keep as a reference during the unit and the next time they go shopping for a sunscreen.

Most of us (hopefully) apply sunscreen to protect us from the sun when we are going to be outside for a long time. But how many of us have ever stopped to read the bottle to see what we are putting on our bodies? What kinds of chemicals are used to block the sun rays? Do different sunscreens use different ingredients to block the sun? How might the different ingredients used affect us? In this activity you'll take a look at several sunscreens to see what we are putting on our bodies when we use these products.

## Materials

- Five different bottles of sunscreen.

To get a diverse group of sunscreens try to use more than one brand. Also see if you can find the following:

- One sunscreen with a high SPF (30-50).
- One sunscreen with a low SPF (5-15).
- One sunscreen designed for skiers or surfers.
- One sunscreen for sensitive skin or babies.
- One sunscreen that has zinc oxide (ZnO) or titanium dioxide ($TiO_2$) as an ingredient. *Note: the proper scientific name for $TiO_2$ is "titanium (IV) oxide", but the older name "titanium dioxide" is more commonly used.*

This activity can be done as homework with a follow up class discussion or as an in-class activity.

As Homework

- Ask your students to visit a local pharmacy or supermarket and do the assignment by looking at the sunscreens they find there. (There is no need for your students to buy any sunscreen.)
- You can ask also each student to research two or three sunscreens and then get together in groups in class to share their results and discuss the questions.
- Before assigning this as homework think about how easy / difficult it will be for your students to get to a pharmacy / supermarket and make sure to allow them enough time to do the assignment.

In-Class

- You will need to either develop your own library of sunscreen products or ask students to bring in products they have lying around at home.
- It is best to use empty sunscreen bottles since the contents of the bottle are not needed for the activity and students may have unknown allergies to some sunscreen ingredients. You can then store the bottles for future use.
- You will want to have a large enough collection and variety of sunscreens so that students aren't waiting to look at the bottles and that they have some choice in what sunscreens to look at.
- It works best to place the sunscreens in stations and have students rotate through them in groups of 2 or 3.

## Instructions

Look at the back of one of the bottles. You should see a list of the "active ingredients" in the sunscreen. These are the ingredients that prevent sunlight from reaching your skin ("inactive ingredients" are added to influence the appearance, scent, texture and chemical stability of the sunscreen.) Also look to see what kind of protection the sunscreen claims to provide. Does it provide UVB protection? UVA protection? Does it claim to have "broad spectrum" protection? What is its SPF number? Does it make any other claims about its protection? Record your observations for each sunscreen in the data chart and then answer the questions that follow.

## Data Chart

| | Brand | Active Ingredients | SPF | UVB? | UVA? | Broad Spectrum? | Price |
|---|---|---|---|---|---|---|---|
| #1 | | | | | | | |
| #2 | | | | | | | |
| #3 | | | | | | | |
| #4 | | | | | | | |
| #5 | | | | | | | |

## Questions

Questions 1 – 5 ask students to review and synthesize the information they recorded from the different sunscreens, students should be able to answer these questions on their own based on the data they recorded.

Questions 6 – 8 are deep thought questions that go beyond the information collected in this activity.

1. How many different active ingredients did most of the sunscreens have?

Most sunscreens will have more than one ingredient.

2. What were the most common active sunscreen ingredients you saw? Are these organic or inorganic ingredients?

Common sunscreen ingredients include:
Homosalate, Octinoxate, Octisalate, Oxybenzone, Octocrylene (All organic)
Zinc Oxide and Titanium Dioxide (Inorganic) are also common sunscreen ingredients.

(also see FDA Approved Sunscreen Ingredient Resource for full list of ingredients)

3. Did any of the sunscreens you looked at have active ingredients that were very different from the rest? If so, what were they?

Avobezone (Parasol 1789) is sometimes added as because of it UVA blocking abilities.
PABA (para aminobenozic acid) is infrequently used because it can irritate skin and stain clothes.
Zinc Oxide and Titanium Dioxide is sometimes found in sunscreens designed for sensitive skin, babies and high SPF ski / surf sunscreens.

4. Were you able to find a sunscreen with inorganic ingredients in it? If so, which one(s) contained them?

Zinc Oxide and Titanium Dioxide (the only 2 FDA approved inorganic ingredients) are often found in sunscreens designed for sensitive skin, babies and high SPF ski / surf sunscreens.

5. How many of your sunscreens claimed to have UVA protection? UVB protection? Broadband protection?

| |
|---|
| Most all sunscreens claim both UVB & UVA protection, but since SPF only measures UVB protection, UVA protection claims currently do not need to be substantiated.<br><br>Broadband protection is a general claim of protection for a wide spread of different wavelength of the electromagnetic spectrum bands. It is usually meant to imply that the sunscreen protects from both UVB (280 – 320 nm) and UVA (320 – 400 nm) radiation, however UVA protection is not yet regulated (see above), so this claim does not have to be substantiated. |

6. Why do you think that many sunscreens have more than one active ingredient? Why can't they just put in more of the "best" one?

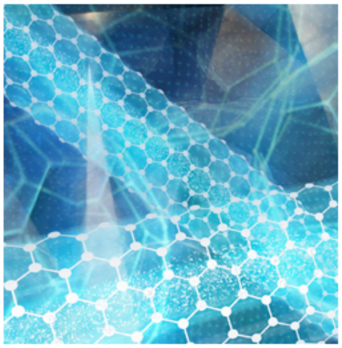
| |
|---|
| Different sunscreen ingredients prevent different wavelengths of light from reaching the skin. They block different parts of the UV spectrum.<br><br>(A secondary reason is that high concentrations of chemicals on the skin can cause irritation, this is why when the FDA approves a sunscreen ingredient, it also lists the maximum concentration that can be used). |

7. You have just looked at a sample of the different chemicals you are putting on your skin when you use sunscreen. Does this raise any health concerns for you? If so, what are some of the things you might be concerned about and why?

| |
|---|
| Irritation / allergies, chemicals getting absorbed by the body and having negative effects on the cells, possibility of getting in eyes, mouth or cuts where there is no skin barrier protection, photoactive chemicals can react with the sun to create free radicals which are known to help cause cancer. |

8. Where could you go to find out more information about possible health concerns?

| |
|---|
| The FDA (Food and Drug Administration http://www.fda.gov/) regulates sunscreen ingredients in the U.S. and provides articles related to their use and safety. There are also many consumer watchgroups who provide information both online and in print. Most sunscreen companies do not publish information about health concerns associated with sunscreen. As with all research, it is important to always evaluate the credibility and potential bias of the author or organization presenting the information.<br><br>You may want to give your students an assignment to search online for information about current health concerns related to nanoparticle use in sunscreens. |



# All About Sunscreens

NanoSense
the basic sense behind nanoscience





## What do Sunscreens Do?

- Sunscreens are designed to protect us by preventing UV rays from reaching our skin
- But what does it mean to **"block"** UV rays?

Source: Image adapted from http://www.ashevilleparc.org/files/sssd1small.jpg

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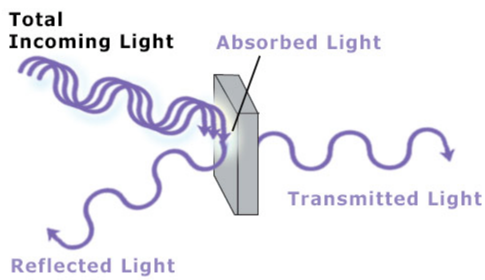
## Light Blocking

- Anytime light interacts with some material, 3 things can happen. The light can be transmitted, it can be reflected, or it can be absorbed




Transmission
Reflection
+ Absorption
100%

- If we say that light is "blocked" it means that it is either absorbed or reflected by the material

Source: Original Image

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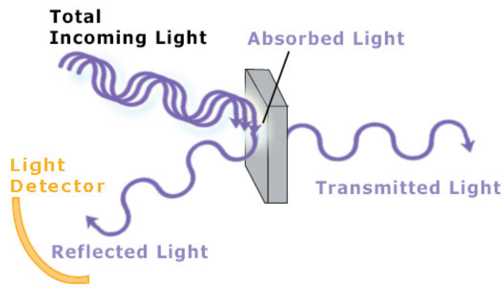
If we know that sunscreens block UV light from reaching our skin does that tell us whether they absorb or reflect the light?

# Sometimes More Experiments Are Needed

- **Both absorption and reflection could explain how sunscreens keep UV light from reaching out skin**
  - To figure out which mechanism is being used, we ran an experiment where we shine UV light on sunscreens and see if we can detect any reflection




**We detected little UV light reflected – so we know that the sunscreens block via absorption**

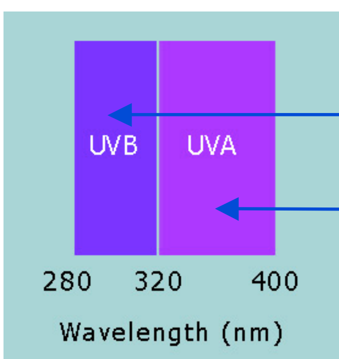
Source: Original Image



# A Brief History of Sunscreens: The Beginning

- **First developed for soldiers in WWII (1940s) to absorb "sunburn causing rays"**

WWII soldiers in the sun




The sunburn causing rays were labeled as UV-B

Longer wavelengths in the UV range were called UV-A

Sources: http://www.bbc.co.uk/wiltshire/content/articles/2005/05/05/peoples_war_feature.shtml
http://www.arpansa.gov.au/is_sunys.htm

# A Brief History of Sunscreens: The SPF Rating

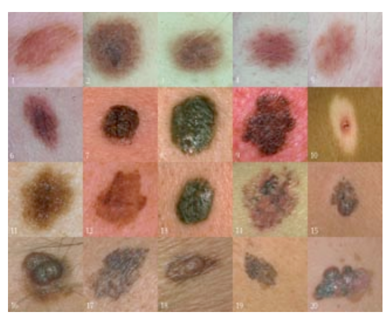
- **Sunscreens first developed to prevent sunburn**
  - Ingredients were good UVB absorbers
- **SPF Number (Sunburn Protection Factor)**
  - Measures the strength of UVB protection only
  - Higher SPF # = more protection from UVB
  - Doesn't tell you anything about protection from UVA


Sources: http://www.shop.beautysurg.com/ProductImages/skincare/14521.jpg and http://www.shop.beautysurg.com/ProductImages/skincare/14520.jpg



# A Brief History of Sunscreens: The UVA Problem

- **UVA rays have no immediate visible effects but cause serious long term damage**
  - Cancer
  - Skin aging
- **Sunscreen makers working to find UVA absorbers**



Twenty different skin cancer lesions

- ***NEW:* The FDA has just proposed a 4-star UVA rating to be included on sunscreen labels!**

Low ★★★★ Med ★★★★ High ★★★★ Highest★★★★

Source: http://www.cs.wright.edu/~agoshtas/fig8.jpg

# How do you know if your sunscreen is a good UVA blocker?



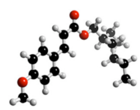
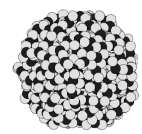
# Know Your Sunscreen: Look at the Ingredients

- **UV absorbing agents suspended in a lotion**
  - "Colloidal suspension"
- **Lotion has "inactive ingredients"**
  - Don't interact w/ UV light
- **UV absorbing agents are "active ingredients"**
  - Usually have more than one kind present


- **Two kinds of active ingredients**
  - Organic ingredients and inorganic ingredients

Source: Original Image

# Sunscreen Ingredients Overview

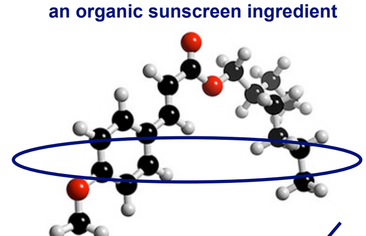
| | Organic Ingredients | Inorganic Ingredients |
|---|---|---|
| Atoms Involved | Carbon, Hydrogen, Oxygen, Nitrogen | Zinc, Titanium, Oxygen |
| Structure (not drawn to scale) | Individual molecule  | Clusters of various size  |
| UV Blocking | Absorb specific bands of UV light | Absorb all UV with $\lambda$ < critical value |
| Appearance | Clear | Large clusters = White<br>Small clusters = Clear |

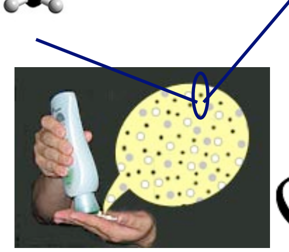


# Organic Ingredients: The Basics

- **Organic = Carbon Compounds**
  - H, O & N atoms often involved
- **Structure**
  - Covalent bonds
  - Exist as individual molecules
- **Size**
  - Molecular formula determines size (states the number and type of atoms in the molecule)
  - Typically a molecule measures a few to several dozen Å (<10 nm)

Octyl methoxycinnamate ($C_{18}H_{26}O_3$)
an organic sunscreen ingredient



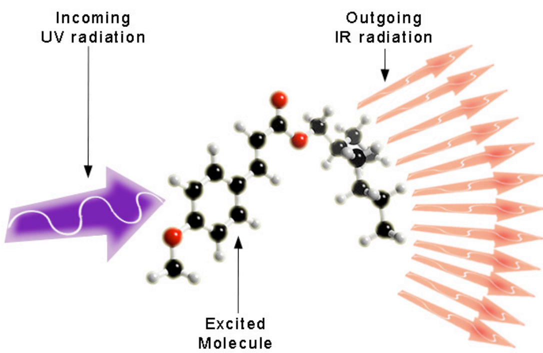


Sources: http://www.3dchem.com/molecules.asp?ID=135# and original image

# Organic Ingredients: UV Blocking

## Organic Sunscreen Ingredients can absorb UV rays

1. Molecules capture energy from the sun's UV rays
2. The energy give the molecule thermal motion (vibrations and rotations)
3. The energy is re-emitted as harmless long wave IR

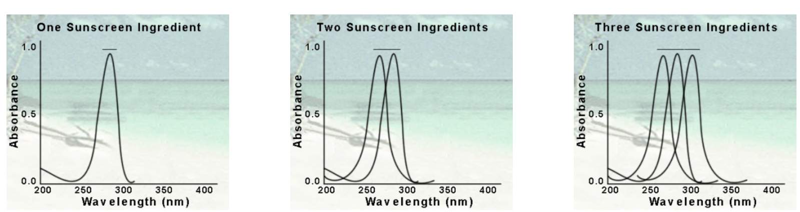



Source: Adapted from http://www.3dchem.com/molecules.asp?ID=135#and http://members.aol.com/WSRNet/tut/absorbu.htm



# Organic Ingredients: Absorption Range

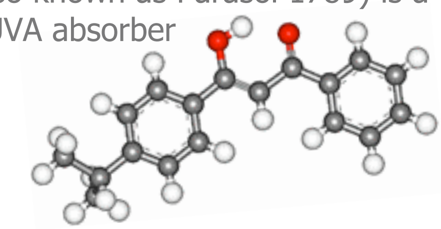
- **Organic molecules only absorb UV rays whose energy matches the difference between the molecule's energy levels**
  - Different kinds of molecules have different peaks and ranges of absorption
  - Using more than one kind of ingredient (molecule) gives broader protection




Source: Graphs adapted from http://www.aims.gov.au/pages/research/projects/sunscreens/pages/sunscreens02.html

## Organic Ingredients: Absorbing UVA / UVB

- **Most organic ingredients that are currently used were selected because they absorb UVB rays**
  - The FDA has approved 15 organic ingredients
  - 13 of these primarily block UVB rays
- **Sunscreen makers are working to develop organic ingredients that absorb UVA rays**
  - Avobenzone (also known as Parasol 1789) is a good FDA approved UVA absorber

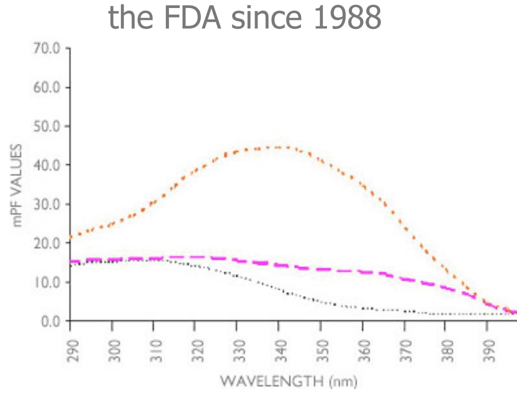


Source: http://jchemed.chem.wisc.edu/JCEWWW/Features/MonthlyMolecules/2004/Oct/JCE2004p1491fig4.gif



## ------Breaking News------

- **Ecamsule (Mexoryl SX) is a new sunscreen ingredient designed to absorb UVA rays**
  - It is the first new sunscreen ingredient approved by the FDA since 1988



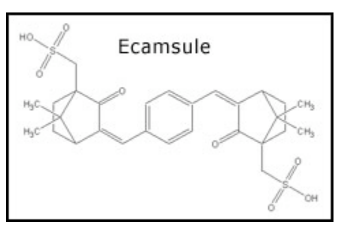




Image Sources: http://www.anthelios.com/anthelios-medical_prof.html and http://en.wikipedia.org/wiki/Image:Mexorylsx.png

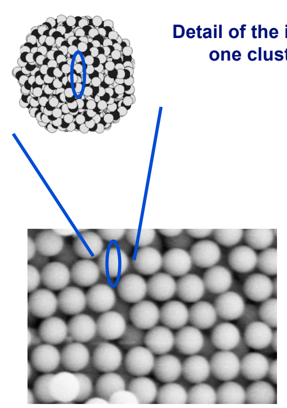
## How are inorganic sunscreen ingredients different from organic ones?

## How might this affect the way they absorb UV light?



## Inorganic Ingredients: The Basics

- **Atoms Involved**
  - Zinc or Titanium
  - Oxygen
- **Structure**
  - Ionic attraction
  - Cluster of ions
  - Formula unit doesn't dictate size
- **Size**
  - Varies with # of ions in cluster
  - Typically ~10 nm – 300 nm



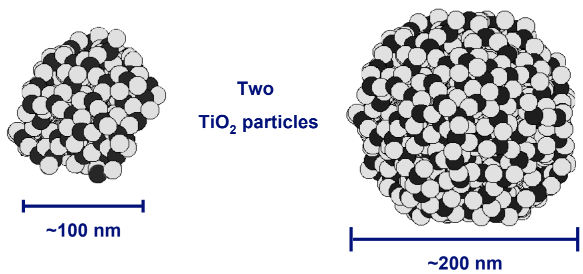
Detail of the ions in one cluster

Group of $TiO_2$ particles

Source: http://www.microspheres-nanospheres.com/Images/Titania/TIO2%20P7.jpg and image adapted from http://www.cse.clrc.ac.uk/msi/projects/ropa.shtml

# Inorganic Ingredients: Cluster Size

- **Inorganic ingredients come in different cluster sizes (sometimes called "particles")**
  - Different number of ions can cluster together
  - Must be a multiple of the formula unit
    - ZnO always has equal numbers of Zn and O atoms
    - $TiO_2$ always has twice as many O as Ti atoms

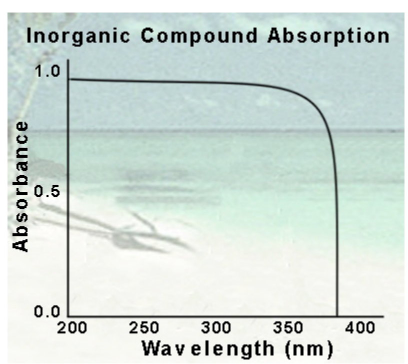



Source: Images adapted from http://www.cse.clrc.ac.uk/msi/projects/ropa.shtml



# Inorganic Ingredients: UV Blocking

- **Inorganic Sunscreen Ingredients can also absorb UV rays**
  - But a different structure leads to a different absorption mechanism
  - Absorb consistently through whole UV range up to ~380nm
  - How is the absorption pattern different than for organics?




Source: Graph adapted from http://www.aims.gov.au/pages/research/projects/sunscreens/pages/sunscreens02.html

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## If inorganic sunscreen ingredients block UVA light so well, why doesn't everybody use them?

Source: http://www.loc.gov/rr/scitech/mysteries/images/sunscreen2.jpg

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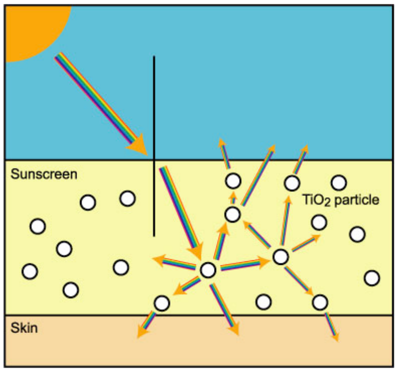
## Appearance Matters

- Traditional inorganic sunscreens appear white on our skin
- Many people don't like how this looks, so they don't use sunscreen with inorganic ingredients
- Of the people who do use them, most apply too little to get full protection

Source: http://www.4girls.gov/body/sunscreen.jpg

## Why Do They Appear White? I

- Traditional ZnO and $TiO_2$ clusters are large
  - (> 200nm)
- Large clusters can scatter light in many different directions
- Maximum scattering occurs for wavelengths twice as large as the cluster
  - $\lambda$ > 400 nm
  - This is **visible** light!



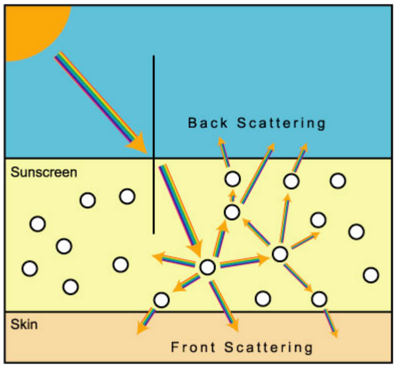

Source: Original Image



## Why Do They Appear White? II

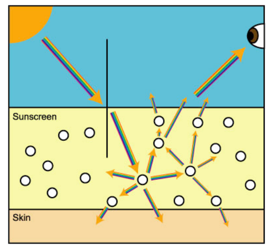
**Light eventually goes in one of two directions:**

1. **Back the way it came (back scattering)**
   - Back-scattered light is reflected
2. **Forwards in the same general direction it was moving (front scattering)**
   - Front-scattered light is transmitted

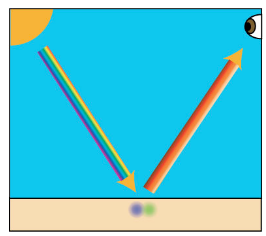


## Why Do They Appear White? III

- **When reflected visible light of all colors reaches our eyes, the sunscreen appears white**




- **This is very different from what happens when sunlight is reflected off our skin directly**
  - Green/blue rays absorbed
  - Only red/brown/yellow rays reflected





## Why don't organic sunscreen ingredients scatter visible light?

Source: Adapted from http://www.loc.gov/rr/scitech/mysteries/images/sunscreen2.jpg

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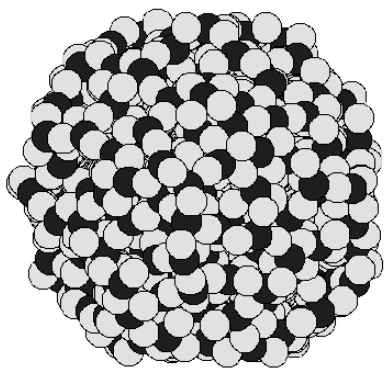
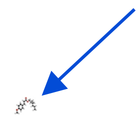
## Organic Sunscreen Molecules are Too Small to Scatter Visible Light



200 nm $TiO_2$ particle
(Inorganic)



Methoxycinnamate (<10 nm)
(Organic)

Source: Images adapted from http://www.cse.clrc.ac.uk/msi/projects/ropa.shtml and http://www.3dchem.com/molecules.asp?ID=135#

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## What could we do to inorganic clusters to prevent them from scattering visible light?

Source: Adapted from http://www.loc.gov/rr/scitech/mysteries/images/sunscreen2.jpg

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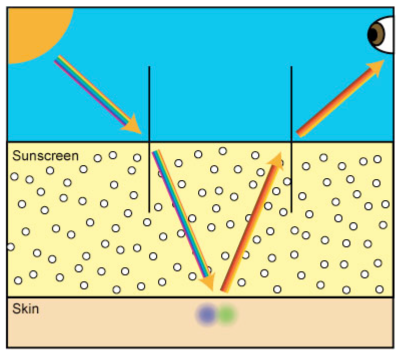
## Nanosized Inorganic Clusters

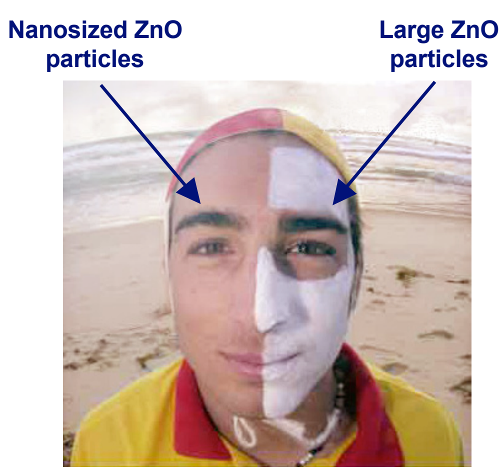
- **Maximum scattering occurs for wavelengths twice as large as the clusters**
  - Make the clusters smaller (100 nm or less) and they won't scatter visible light




Source: Graph adapted from http://www.aims.gov.au/pages/research/projects/sunscreens/pages/sunscreens02.html

NanoSense 30

## Nano-Sunscreen Appears Clear




Source: http://www.science.org.au/sats2003/images/barber-slide3.jpg

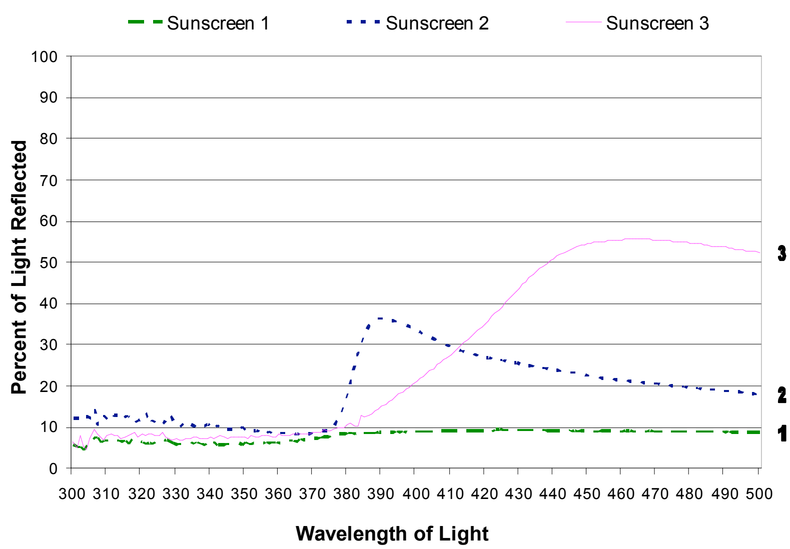
## Let’s Look at Some Real Data…

- **Three sunscreens were tested for reflection (back-scattering) with different wavelengths of light**
  - One contains nanosized inorganic ingredients
  - One contains traditional inorganic ingredients
  - One contains organic ingredients

- **Answer the following questions for each sunscreen:**
  1. Will it appear white or clear on your skin?
  2. What size (approximately) are the molecules / clusters?
  3. Can we tell how good a UV blocker it is from this graph? Why/ why not?
  4. Which one of the sunscreens is it? How do you know?



## Light Reflected by Three Sunscreens



# In Summary I

| | Organic Ingredients | Inorganic Ingredients (Nano) | Inorganic Ingredients (Large) |
|---|---|---|---|
| Structure | Individual molecule | Cluster ~100 nm in diameter | Cluster > 200 nm in diameter |
| Interaction w/ UV light | Absorb specific $\lambda$ of UV light | Absorb all UV < critical $\lambda$ | Absorb all UV < critical $\lambda$ |
| Absorption Range | Parts of UVA or UVB spectrum | Broad spectrum, both UVA and UVB | Broad spectrum, both UVA and UVB |
| Interaction w/Vis light | None | None | Scattering |
| Appearance | Clear | Clear | White |



# In Summary II

- **Nanoparticle sunscreen ingredients are small inorganic clusters that:**
  - Provide good UV protection by absorbing most UVB and UVA light
  - Appear clear on our skin because they are too small to scatter visible light

Source: http://www.smalltimes.com/images/st_advancednanotech_inside_.jpg

# Essential Questions: Time for Answers

1. What are the most important factors to consider in choosing a sunscreen?

2. How do you know if a sunscreen has “nano” ingredients?

3. How do “nano” sunscreen ingredients differ from other ingredients currently used in sunscreens?

# All About Sunscreens: Teacher Notes

## Overview

This series of slides discusses the basics of sunscreens including their history, types, mechanism for blocking UV light (absorption), appearance (due to scattering) and challenges to providing effective protection. The final slide asks students to use what they've learned to answer the three driving questions for the unit.

Slide 14 includes an optional demo that shows how selective absorption of UV light by certain chemicals used in printing money is serves as an anti-counterfeiting measure. If you choose to do this demo you will need:

- One or more UV lights of any size (several options are available from Educational Innovations at www.teachersource.com)
- Different kinds of paper currency (these must be relatively recently printed; Euros and Canadian bills work particularly well)

## Slide 1: Title Slide

## Slide 2: What do Sunscreens Do?

This slide is designed to get students thinking about how sunscreens protect our skin. Have students brainstorm ideas about what might happen to the UV rays when they encounter the sunscreen. Ask them how they could test their ideas to see if they are correct.

## Slide 3: Light Blocking

The T + R + A = 100% equation is based on the conservation of energy. All incoming light (energy) must be accounted for. It either passes through the material, is sent back in the direction from which it came or is absorbed by the material.

**Analogy:** The R + T + A = 100% equation can be thought of in terms of baseball. When a pitcher throws the ball towards the batter, three things can happen. The batter can hit the ball (reflection), the catcher can catch the ball (absorption), or the ball can pass by both of them (transmission).

## Slide 4: If we know that sunscreens block UV light from reaching our skin does that tell us whether they absorb or reflect the light? (Question Slide)

Have your students brainstorm ideas about we could figure out what happens to the light. You may need to remind them that the question asks about UV light (which is not visible to the human eye). Assuming we had a UV light detector, where would we want to put it and what would we expect it to measure for each possible scenario (absorption and reflection)?

## Slide 5: Sometime More Experiments Are Needed

A key point of this slide is that there are often multiple valid theoretical explanations for experimental data; to find out which works best, additional experiments are required.

For example, it is well known that sunscreens "block" UV light, but this could be viably explained by either absorption or reflection.

To find out which explanation was a better fit for the "blocking" phenomenon, we conducted an experiment in which we prepared a series of glass slides covered with sunscreens. We shone UV light on the sunscreens and placed UV light detectors both on the other side of the slide (to measure transmitted light) and next to the original light source (to measure reflected light). Little reflected or transmitted UV light was detected, so we can infer from T + R + A =100% that the sunscreen is absorbing the UV light.

Note that it is often possible to engineer useful materials with an incomplete understanding of their properties. In this example we can design sunscreens that provide effective protection against UV light without knowing whether they do so via absorption or reflection.

## Slide 6: A Brief History of Sunscreens: The Beginning

Sunscreens were developed to meet a specific and concrete need: prevent soldiers from burning when spending long hours in the sun. Scientists applied their knowledge of how light interacts with certain chemicals to develop products to meet this need.

The division of the continuous UV spectrum into UVA and UVB categories is somewhat arbitrary. The UVB range is talked about as starting at around 280-290 nm at the lower end and ending around 310-320 nm at the upper end.

## Slide 7: A Brief History of Sunscreens: The SPF Rating

SPF (Sunscreen Protection Factor) values are based on an "in-vivo" test (done on human volunteers) that measures the redness of sunscreen-applied skin after a certain amount of sun exposure.

SPF used to be thought of a multiplier that can be applied to the time taken to burn, but this is not done anymore because there are so many individual differences and other variables that change this equation (skin type, time of day, amount applied, environment, etc.)

The FDA recommends always using sunscreens with an SPF of at least 15 and not using sunscreen as a reason to stay out in the sun longer. Remind students that no sunscreen can prevent all possible skin damage.

**Common Student Question:** Is it true that sunscreens above SPF 30 don't provide any extra protection?

**Answer:** No, this is not true. However, since SPF is not based on a linear scale, a sunscreen with an SPF of 40 does not provide twice as much protection as a sunscreen with an SPF of 20. Even though you don't get double the protection, you do get some additional protection and so there is added value in using SPFs above 30.

In the past the FDA only certified SPFs up to 30 but didn't confirm the reliability of higher claims by sunscreen manufacturers. Recently, due to improvement in testing procedures, the FDA had proposed certifying results up to and SPF of 50.

### Slide 8: A Brief History of Sunscreens: The UVA Problem

Since there is no immediate visible effect, it is relatively recently that we have come to understand the dangers of UVA rays. In August 2007, the FDA proposed a UVA rating to be included on sunscreen labels; as of December 2007, the proposal was still under discussion. If the FDA proposal is passed, sunscreen manufacturers will have 18 months to comply with the new labeling requirements.

Creating a rating for UVA protection has been difficult for two reasons:

1. Since UVA radiation does not lead to immediate visible changes in the skin (such as redness) what should be the outcome measure? Is it valid to do an "in-vitro" (in a lab and not on a human) test? *(The FDA proposal includes both)*

2. How should the UVA protection level be communicated to consumers without creating confusion (with the SPF and how to compare / balance the two ratings)? *(The FDA proposal uses a 4-star system)*

Creating a UVA blocking rating is important since without immediate harmful effects, people are not likely to realize that they have not been using enough protection until serious long term harm has occurred.

### Slide 9: How do you know if your sunscreen is a good UVA blocker? (Question Slide)

Have your students brainstorm ideas about ways to tell if a sunscreen is a good UVA blocker.

### Slide 10: Know Your Sunscreen: Look at the Ingredients

"Formulating" a sunscreen is the art of combing active and inactive ingredients together into a stable cream or gel product. One of the important challenges here is creating a stable suspension with even ingredient distribution. If the active ingredients clump together in large groups then the sunscreen provides strong protection in some areas and little protection in others.

**Analogy:** Students may be familiar with the suspension issue as it relates to paint. If paint has been sitting for a while and it is used directly, a very uneven color is produced. This is why we stir (or shake) paint before using in order to re-suspend the particles.

Another issue in sunscreen formulation is trying to create a product that customers will want to buy and use. Qualities such as smell, consistency and ease of rubbing into the skin all play a role in whether or not a sunscreen will be used and whether it will be used in sufficient quantity.

### Slide 11: Sunscreen Ingredients Overview

This slide is an advance organizer for the content of the rest of the slide set. You may wish to give your students the Overview of Sunscreen Ingredients: Student Handout at this point to refer to during the rest of the presentation.

You do not need to discuss the details of each cell at this point in the presentation, simply point out that organic and inorganic ingredients have several different properties that will be discussed. All of the content of the table is explained in detail in the following slides.

### Slide 12: Organic Ingredients: The Basics

The full name of the compound shown is octyl methoxycinnamate (octyl refer to the eight carbon hydrocarbon tail shown on the right side of the molecule) but it is commonly referred to as octinoxate or OMC.

### Slide 13: Organic Ingredients: UV Blocking

When a molecule absorbs light, energy is converted from an electromagnetic form to a mechanical one (in the form of molecular vibrations and rotations). Because of the relationship between molecular motion and heat, this is often referred to as thermal energy.

The process of releasing the absorbed energy is called relaxation. While atoms which have absorbed light simply re-emit light of the same wavelength/energy, molecules have multiple pathways available for releasing the energy. Because of the many vibrational and rotational modes available, there are many choices for how to relax. Since these require smaller energy transitions than releasing the energy all at once, they provide an easier pathway for relaxation – this is why the energy absorbed from the UV light is released as harmless (low energy) IR radiation.

### Slide 14: Organic Ingredients: Absorption Range

Light absorption by molecules is similar to the emission of light by atoms with three key differences:

- Light is captured instead of released.
- Molecules absorb broader bands of wavelengths than atoms because there are multiple vibrational and rotational modes to which they can transition (for more details on molecular absorption concepts, see the Lesson 3 PPT and teacher notes).
- There are multiple pathways for relaxation – the light emitted does not have to be the same wavelength as the light absorbed.

Different molecules have different peak absorption wavelengths, different ranges of absorption and differences in how quickly absorption drops off (“fat” curves as compared to “skinny” ones). It is important to realize that even within a molecule’s absorption range, it does not absorb evenly and absorption at the ends of the range is usually low. For example, octyl methoxycinnamate has an absorption range of 295-350 nm, but we would not expect it to be a strong absorber of light with a wavelength of 295 nm.

**UV Absorption Demonstration:** As one effort to prevent the circulation of counterfeit currency, bills are often printed with special chemicals that absorb specific wavelengths of UV light (this occurs because the energy of these UV rays matches the difference between the molecule's energy levels). When one of these bills is held under a UV light, these molecules absorb the UV light and reemit purple light in the visible spectrum that we can see (note that that the remitted light is not UV light which is not visible to the human eye). You can demonstrate this effect for your students by turning off the classroom lights and shining a UV light on different kinds of bills and watching the printed designs appear (these must be relatively recently printed; Euros and Canadian bills have particularly interesting designs). If you have two UV lights of different wavelengths, you may even be able to see two different designs due to the selective absorption of the different molecules used in the printing.

### Slide 15: Organic Ingredients: Absorbing UVA / UVB

Many organic ingredients block "shortwave" UVA light (also called UVA 2 light and ranging from ~320 to 340 nm) but not "longwave" UVA light (also called UVA 1 light and ranging from ~340 to 400 nm). Up till 2006, avobenzone was the only organic ingredient currently approved by the FDA that is a good blocker of longwave UVA light.

### Slide 16: Breaking News

In the summer of 2006, the FDA approved Ecamsule (Mexoryl SX), a new sunscreen ingredient designed to absorb UVA rays. One benefit of this ingredient is that it is photo-stable (many sunscreens are degraded by the sun), but since it is water soluble, it does not provide protection in the water.

This is the first new ingredient to be approved by the FDA since 1998; however it has been approved in Europe since 1991. There is a great deal of pressure on the FDA to approve several other sunscreen ingredients that are already approved in Europe.

**Graph Q & A for students:**

- What does the y-axis shows? (% absorption)
- What kinds of wavelengths does this ingredient absorb? (UVA up to ~360 nm)
- Is this an organic ingredient? (Yes)
- How do you know? (Molecular structure with carbon, hydrogen, and nitrogen)

### Slide 17: How are inorganic sunscreen ingredients different from organic ones? How might this affect the way they block UV light? (Question Slide)

Have your students brainstorm how inorganic sunscreens might be different from organic ones and how this might affect the way they block UV light.

### Slide 18: Inorganic Ingredients: The Basics

Inorganic compounds are described by a formula unit instead of a molecular formula. The big difference is that while a molecular formula tells you exactly how many of each kind of atom are bonded together in a molecule; the formula unit only tells you the ratio between the atoms. Thus while all molecules of an organic substance will have exactly the same number of atoms involved (and thus be the same size), inorganic clusters can be of any size as long as they have the correct ratio between atoms. This occurs because inorganic substances are held together by ionic, not covalent bonds.

You may want to review some of the basics of bonding in inorganic compounds (electrostatic attraction between ions) as opposed to bonding in organic molecules (electron sharing via covalent bonds) with your students here.

### Slide 19: Inorganic Ingredients: Cluster Size

*Note: the proper scientific name for $TiO_2$ is "titanium (IV) oxide", but the older name "titanium dioxide" is more commonly used.*

This slide is a re-emphasizes the difference between a molecular formula and the formula unit of an inorganic substance. While the molecular formula indicates the <u>actual</u> number of atoms that combine together to form a molecule, the formula unit indicates the <u>ratio</u> of atoms that combine together to form an inorganic compound. Molecules are always the same size whereas inorganic compounds can vary in the number of atoms involved and thus the size of the cluster.

**Common Confusion:** Inorganic compound clusters are often referred to informally as "particles". Students often confuse this use of the word particle with the reference to the sub-atomic particles (proton, electrons and neutrons) or with reference to a molecule being an example of a particle.

### Slide 20: Inorganic Ingredients: UV Blocking

When an inorganic compound absorbs light, energy is converted from an electromagnetic form to a mechanical one (kinetic energy of electrons). The excited electrons use this kinetic energy to "escape" the attraction of the positively charged nuclei and roam more freely around the cluster.

Because there are so many more atoms involved in an inorganic compound than in a molecule, there are also many more different energy values that electrons can have (students can think of these loosely as how "free" the electrons are to move about the cluster; how far from their original position they can roam). The greater number of possible energy states means that a greater range of wavelengths of UV light can be absorbed leading to the broader absorption spectrum shown in the graph.

### Slide 21: If inorganic sunscreens ingredients block UVA light so well, why doesn't everybody use them? (Question Slide)

Have your students brainstorm reasons why sunscreen manufacturers and consumers might not want to use inorganic sunscreen ingredients.

### Slide 22: Appearance Matters

One of the major reasons that people have not used inorganic ingredients in the past is because of their appearance. Before we knew how dangerous UVA rays were, sunscreens with organic ingredients seemed to be doing a good job (since they do block UVB rays).

Applying too little sunscreen is very dangerous because this reduces a sunscreen's blocking ability while still giving you the impression that you are protected. In this situation people are more likely to stay out in the sun longer and then get burned.

### Slide 23: Why Do They Appear White? I

Scattering is a physical process that depends on cluster size, the index of refraction of the cluster substance and the index of refraction of the suspension medium. No energy transformations occur during scattering (like they do in absorption); energy is simply redirected in multiple directions. The wavelengths (and energy) of light coming in and going out are always the same.

Maximum scattering occurs when the wavelength is twice as large as the cluster size. Since traditional inorganic sunscreen ingredients have diameter > 200 nm, they scatter light which is > 400 nm in diameter – this is in the visible spectrum.

### Slide 24: Why Do They Appear White? II

Multiple scattering is a phenomenon of colloids (suspended clusters). When light is scattered, at the micro level it goes in many directions. At the macro level, it eventually either goes back the way it came or forwards in the same general direction it was moving. These are known as back- and front- scattering and they contribute to reflection and transmission respectively.

Note that the formula presented earlier (Reflection + Transmission + Absorption = 100%) still holds. Scattering simply contributes to the "reflection" and "transmission" parts of the equation. (For more details on scattering concepts, see the Lesson 4 PPT and teacher notes).

### Slide 25: Why Do They Appear White? III

The scattering of visible light by ZnO and $TiO_2$ is the cause of the thick white color seen in older sunscreens. When the different colors of visible light are scattered up and away by the sunscreen, they reach our eyes. Since the combination of the visible spectrum appears white to our eyes, the sunscreen appears white.

Depending on your students' backgrounds, you may want to review how white light is a combination of all colors of light.

You may also want to discuss how the pigment in our skin selectively absorbs some colors (wavelengths) of visible light, while reflecting others. This is what usually gives our skin its characteristics color. Different pigments (molecules) absorb different wavelengths; this is why different people have different color skin.

### Slide 26: Why don't organic sunscreen ingredients scatter visible light? (Question Slide)

Have your students brainstorm reasons why organic sunscreen ingredients don't scatter visible light.

## Slide 27: Organic Sunscreen Molecules are Too Small to Scatter Visible Light

Traditional inorganic clusters are usually 200 nm or larger, causing scattering in the visible range (400-700 nm). Organic sunscreen molecules are smaller than 10 nm (usually 1-20 Angstroms) and thus do not scatter in the visible range.

You may want to talk about how while the individual organic sunscreen molecules are very small compared to inorganic sunscreen clusters (many formula units ionically bonded together creating a large cluster) and the wavelengths of visible light, they are big compared to many of the simple molecules that students are used to studying, such as water or hydrochloric acid.

How big or small something seems is relative to what you are comparing it to. In this case, we are comparing sunscreen ingredients with the size of the wavelength of light.

## Slide 28: What could we do to inorganic clusters to prevent them from scattering visible light? (Question Slide)

Have your students brainstorm what we could do to inorganic clusters to prevent them from scattering light. If students say "make them smaller", ask them how small the clusters would need to be in order to not scatter visible light.

## Slide 29: Nanosized Inorganic Clusters

When visible light is not scattered by the clusters, it passes through the sunscreen and is reflected by our skin (blue and green rays are absorbed by pigments in the skin and the red, yellow and orange rays are reflected to our eyes giving skin its characteristic color).

Changing the size of the cluster does not affect absorption since this depends on the energy levels in the substance which are primarily determined by the substance's chemical identity.

**Discussion Question for Students:** Is it good or necessary to block visible light from reaching our skin?

**Answer:** Visible light has less energy than UVA light and is not currently thought to do any harm to our skin thus there is no need to block it. Think about human vision: visible light directly enters our eyes on a regular basis without causing any harm.

**If you are not planning on doing Lesson 4:** You may want to demo the sunscreen animations for your class at this point. The animations are available at http://nanosense.org/activities/clearsunscreen/index.html and are explained in the Sunscreens & Sunlight Animations: Teacher Instructions & Answer Key in Lesson 4.

## Slide 30: Nano-Sunscreen Appears Clear

This slide shows the difference in appearance between traditional inorganic and nanosunscreens.

## Slide 31: Let's Look at Some Real Data…

At this point you should hand out the Light Reflection by Three Sunscreens: Student Worksheet. You can either have students work on it in groups or proceed to the next slide and work through the questions as a whole class.

## Slide 32: Light Scattering by Three Sunscreens

The following answers are also presented in chart form in the Light Reflection by Three Sunscreens: Teacher Answer Key.

**Sunscreen 1**

*Appearance*

- No scattering in the visible range
- Sunscreen appears clear on the skin.

*Size*

- Since no scattering seen, it is not possible to estimate the size of the molecule from the information in the graph.

*UV Blocking*

- The graph shows very little reflection in the UV range, however, this doesn't tell us anything because absorption is the main blocking mechanism for UV.
- We would need an absorption or transmission graph in order to determine the UV blocking ability of the sunscreens.
- T + R + A = 1

*Identity*

- Virtually no scattering in the visible range indicates organic ingredients.
- Because organic molecules are small compared to the wavelengths of light used, almost no scattering in the visible range occurs and the line is basically flat.
- This sunscreen contains the organic ingredients octinoxate (shown on slides 9 & 10) and oxybenzone.
- (The sunscreen is Walgreens SPF 15).

**Sunscreen 2**

*Appearance*

- Very limited scattering in the visible range
- Sunscreen appears clear on the skin.

*Size*

- The sharp drop in the curve at 380 nm is actually due to absorption (if all the light is getting absorbed, it can't be scattered) so we cannot know the exact size of the cluster.
- We only know that the curve would have peaked below 380 nm, so the cluster size is smaller than 190 nm.

*UV Blocking*

- See general explanation under Sunscreen 1.

*Identity*

- Low amounts of scattering in the visible range, indicates inorganic ingredients with nanosized clusters.
- Because nanosized clusters are less than half the size of the wavelengths of light used, limited scattering in the visible range occurs.
- This sunscreen contains nanosized zinc oxide.
- (The sunscreen is Skin Ceuticals SPF 30).

**Sunscreen 3**

*Appearance*

- Significant scattering in the visible range.
- Sunscreen appears white on the skin.

*Size*

- Significant scattering in the visible range.
- Sunscreen appears white on the skin.

*UV Blocking*

- See general explanation under Sunscreen 1.

*Identity*

- Significant amounts of scattering in the visible range indicates inorganic ingredients with large clusters size.
- Because traditional inorganic ingredient clusters are about half the size of the wavelengths of light used, a great deal of scattering in the visible range occurs.
- This sunscreen contains traditional titanium dioxide.
- (The sunscreen is Bullfrog SPF 45).

## Slide 33: In Summary I

If you have not yet given your students the Overview of Sunscreen Ingredients: Student Handout, do so now. Use the handout to review the similarities and differences between the three kinds of ingredients.

**Key Similarities & Differences:**

- Both kinds of inorganic ingredients have the same atoms, structure and UV absorption
- Nano-inorganic clusters are much smaller than the cluster size of traditional inorganic ingredients, thus do not scatter visible light, thus are clear.

## Slide 34: In Summary II

The big benefit of nano-sunscreen ingredients is that they combine UVA blocking power with an acceptable appearance.

## Slide 35: Essential Questions: Time for Answers

Hand out the Reflecting on the Guiding Questions: Student Worksheet and have students work in pairs to answer it. You may also want to review the questions with the class as a whole.

# Light Reflection by Three Sunscreens: Teacher Answer Key

## Introduction

Three sunscreens were tested for reflection (back-scattering) with different wavelengths of light:

- One contains nanosized inorganic ingredients
- One contains traditional inorganic ingredients
- One contains organic ingredients

A graph was created to show the percent of light reflected by each sunscreen at different wavelengths and is included in this packet.

## Instructions

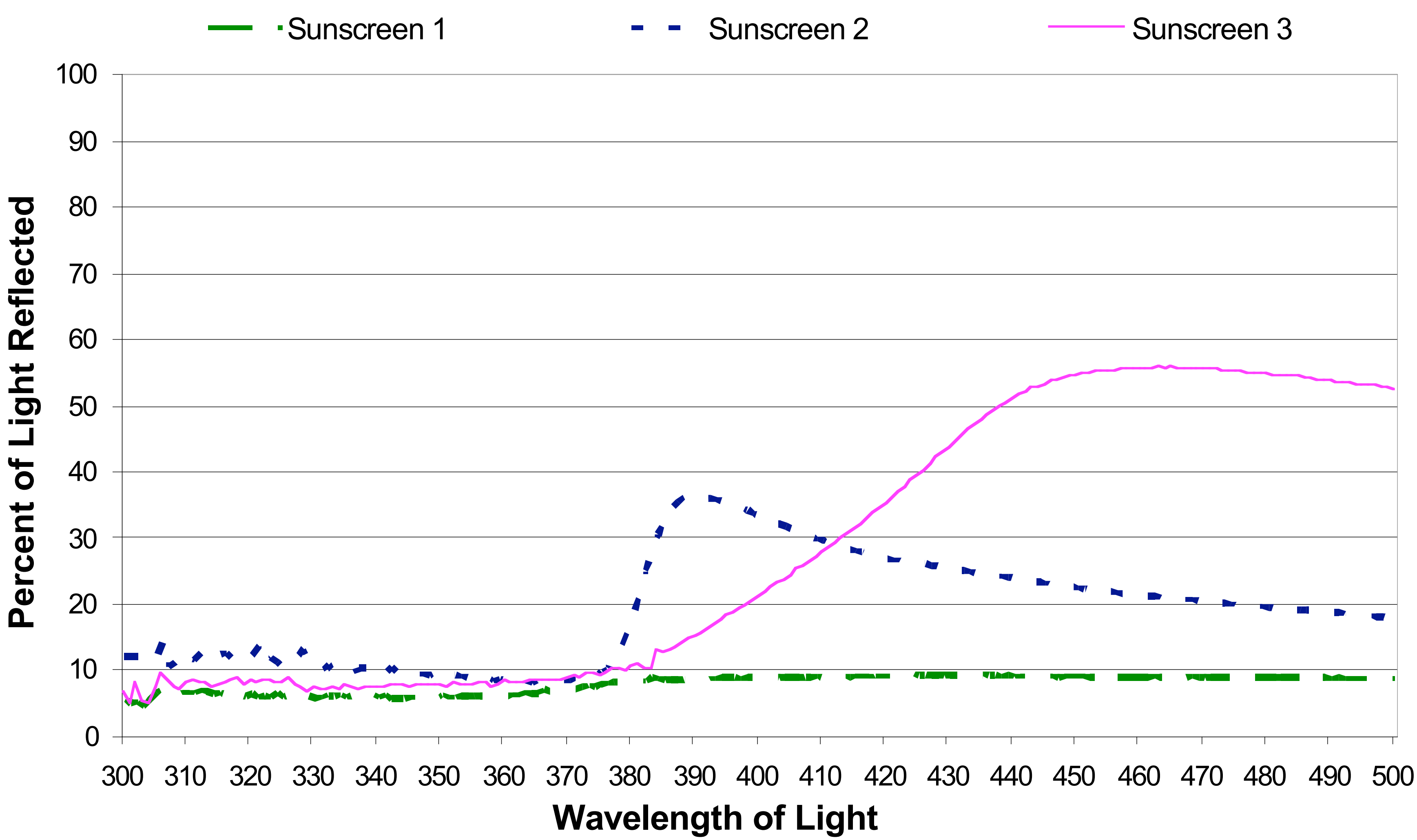
Use the graph to answer the following questions for each sunscreen in the chart on the next page:

1. Will it appear white or clear on your skin? How do you know?
2. What size (approximately) are the molecules / clusters?
3. Can we tell how good a UV blocker it is from this graph? Why/ why not?
4. Which one of the sunscreens is it? How do you know?

**Light Reflection by Three Sunscreens Chart**

| | Appearance | Size | UV Blocking | Identity (w/ reason) |
|---|---|---|---|---|
| **# 1** | No scattering in the visible range<br>Sunscreen appears clear on the skin. | Since no scattering seen, it is not possible to estimate the size of the molecule from the information in the graph. | The graph shows very little reflection in the UV range, however, this doesn't tell us anything because absorption is the main blocking mechanism for UV.<br>We would need an absorption or transmission graph in order to determine the UV blocking ability of the sunscreens.<br>$T + R + A = 1$ | Virtually no scattering in the visible range indicates organic ingredients.<br>Because organic molecules are small compared to the wavelengths of light used, almost no scattering in the visible range occurs and the line is basically flat.<br>This sunscreen contains the organic ingredients octinoxate (shown on slides 9 & 10) and oxybenzone.<br>(The sunscreen is Walgreens SPF 15). |
| **# 2** | Very limited scattering in the visible range<br>Sunscreen appears clear on the skin. | The sharp drop in the curve at 380 nm is actually due to absorption (if all the light is getting absorbed, it can't be scattered) so we cannot know the exact size of the cluster.<br>We only know that the curve would have peaked below 380 nm, so the cluster size is smaller than 190 nm. | See above. | Low amounts of scattering in the visible range, indicates inorganic ingredients with nanosized clusters.<br>Because nanosized clusters are less than half the size of the wavelengths of light used, limited scattering in the visible range occurs.<br>This sunscreen contains nanosized zinc oxide.<br>(The sunscreen is Skin Ceuticals SPF 30) |
| **# 3** | Significant scattering in the visible range.<br>Sunscreen appears white on the skin. | Because the graph peaks around 450 nm, we would estimate the cluster size to be about 225 nm. | See above. | Significant amounts of scattering in the visible range indicates inorganic ingredients with large clusters size.<br>Because traditional inorganic ingredient clusters are about half the size of the wavelengths of light used, a great deal of scattering in the visible range occurs.<br>This sunscreen contains traditional titanium dioxide.<br>(The sunscreen is Bullfrog SPF 45). |

# Light Reflected by Three Sunscreens



# Reflecting on the Guiding Questions: Teacher Instructions & Answer Key (Lesson 2)

You may want to have your students keep these in a folder to use at the end of the unit, or collect them to see how your students' thinking is progressing. You can also have a group discussion about what students learned from the activity that helps them answer the guiding questions.

**Discussion Idea:**

For each "What I still want to know" section, have students share their ideas and discuss whether their questions are scientific ones or questions of another sort. Scientific questions are questions about how the natural world operates that can be answered through empirical experiments. Other kinds of questions might be ethical in nature (e.g. do friends have a responsibility to persuade friends to use sunscreen?) or policy questions (e.g. should the FDA endorse the most effective sunscreens?).

Think about the activities you just completed. What did you learn that will help you answer the guiding questions? Jot down your notes in the spaces below.

1. What are the most important factors to consider in choosing a sunscreen?

What I learned in this activity:

**Possible Answers:**

It is important to choose a sunscreen that provides good protection against both UVA and UVB.

A sunscreen's SPF number tells us how well the sunscreen protects against UVB rays.

Right now there is no regulated measure of UVA protection. Sunscreen labels that claim UVA or "broadband" protection may or may not actually protect against all UVA light.

Until the new FDA UVA rating is approved, the only way to tell how well a sunscreen protects against UVA rays is by looking at the ingredients. Avobenzone and Ecamsule are two organic ingredients that provide protection from some of the UVA range. Zinc Oxide and Titanium Dioxide are two inorganic ingredients that provide protection from almost the whole UVA range.

It is also important to choose a sunscreen that we like in terms of appearance and smell to make sure that we use enough of it to be effective.

What I still want to know:

2. How do you know if a sunscreen has “nano” ingredients?

What I learned in this activity:

**Possible Answers:**

“Nano” ingredients are smaller versions of traditional inorganic ingredients that go on clear. If a sunscreen contains Zinc Oxide or Titanium Dioxide, but appears clear on our skin, then it likely contains nanoparticles of ZnO or $TiO_2$.

What I still want to know:

3. How do “nano” sunscreen ingredients differ from most other ingredients currently used in sunscreens?

What I learned in this activity:

**Possible Answers:**

Most ingredients currently used in sunscreens are organic ingredients. These are individual molecules that absorb narrow bands of the UVA or UVB spectrum.

“Nano” sunscreen ingredients are inorganic and absorb almost the whole UV spectrum.

“Nano” sunscreen ingredients are inorganic and very similar to traditional inorganic ingredients (large ZnO and TiO2 clusters) – they are made up of the same kinds of atoms and have the same formula unit, thus they absorb strongly in both the UVA and UVB range up to their cutoff wavelength: 380nm (ZnO) or 365 nm (TiO2).

What I still want to know: