CHEMMATTERS

December 2003 Teacher's Guide

About the Guide

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Puzzle: Blockbuster

In these two puzzles, there is a grid partially filled in with letters. When the three missing letters are inserted, you'll see words often used in chemistry. You may be able to guess them, but to help out we'll supply a clue for each word.
But there's more. Picking one of the three missing letters in each word will form a phrase reading down that many a chemistry teacher offers to students.
See if you can find it!

Puzzle #1

R		B			E	_____	a five-carbon sugar
W			S	O		_____	cloud chamber inventor
	L	K			I	_____	group 1 metal
U			C	I		_____	one of the nucleic acid bases
	S		M		R	_____	dimethyl ether vs ethanol
E	N				Y	_____	heat, light, electricity, etc

_______________**A redox mnemonic**

Puzzle #2

N	I				C	_____	an oxidizing acid
S		A		C		_____	polymer of glucose
		Q	U	I		_____	one of the phases
C	A		I			_____	a positively charged atom
	E	L	V			_____	temperature scale
	E	L		U		_____	its nucleus is an alpha particle
P			A	S		_____	found in wood ash, source of K
G		Y	C			_____	antifreeze
F		R			C	_____	iron(III)

________ _______**an aid to doing stoichiometry**

Puzzle Answers

Puzzle 1
Ribose, Wilson, Alkali, Uracil, Isomer, Energy
The mnemonic is OIL RIG—oxidation is loss, reduction is gain (of electrons)

Not LEO GER or LEOA GERC, **L**ose **E**lectrons **O**xidation at the **A**node, **G**ain **E**lectrons **R**eduction at the **C**athode.

Puzzle #2
Nitric, Starch, Liquid, Cation, Kelvin, Helium, Potash, Glycol, Ferric
The phrase is THINK MOLE

Student Questions

Vanilla! It's Everywhere!

1. Describe how the *vanilla planifolia* plant is grown, harvested, and turned into vanilla extract.

2. What is the name and formula for the major component of vanilla extract? How many major and minor chemicals are contained in vanilla extract?

3. Describe the differences between "imitation vanilla," "natural vanilla," and true vanilla extract. What achievement made the production of "imitation vanilla" possible?

4. What is ethyl vanillin? How does its properties compare to normal vanillin? In what kind of products is ethyl vanillin most likely to be found?

5. What are some of the medical uses of vanilla?

Teeth Whitening

1. Describe the two outermost layers of a human tooth. Which layer determines the color of a tooth?

2. Where does most tooth discoloration occur? What kinds of materials are put into toothpaste to remove this kind of discoloration?

3. What is the most common chemical used in whitening gels to remove tooth discoloration that occurs below the surface? Describe the basic mechanism by which the discoloration is removed.

4. What are three common ways to bleach your teeth? Describe each of them.

5. Using chemical equations, show how hydrogen peroxide can function as both an oxidizing agent as well as a reducing agent.

Hydrothermal Vents and Giant Tubeworms

1. What is a hydrothermal vent? Why are some of them called "black smokers," and what gives them their appearance?

2. Why doesn't the water in a hydrothermal vent boil, when it can be as hot as 300 ^{o}C?

3. Since no sunlight reaches the area around a hydrothermal vent, photosynthesis cannot support life there, so scientists thought that the creatures living around a hydrothermal vent must be living off of food and debris falling from higher parts of the ocean. What simple observation argues against this assumption? Explain why.

4. Describe the kinds of observations made on tubeworms that gave scientists a hint as to how they were obtaining their source of food.

5. Describe the general way that sulfur bacteria fix carbon in a manner that parallels photosynthesis.

The Mystery of The Pockmarked Paint Job

1. What are "secondary electrons?" How are they produced in a scanning electron microscope?

2. How is the image produced by a scanning electron microscope created?

3. How are X-rays produced inside a scanning electron microscope?

4. What kind of information can be obtained from studying the X-rays emitted from a specimen in a scanning electron microscope?

5. What are backscattered electrons?

6. What is the most important information obtained about a sample from studying the backscattered electrons?

Answers to Student Questions

Vanilla! It's Everywhere!

1. The *vanilla planifolia* plant produces an orchid flower that opens for only one day. Workers using a bamboo stick pollinate it. Each plant is so valuable that it is guarded and sometimes tattooed with its own I.D. number. The plant produces large pods, which are picked while still green. They must then be "killed" in hot water, "sweated" in the sun, dried in the shade and "conditioned" in a closed box until they turn brown, supple, and fragrant. This process promotes enzymatic action which develops the vanilla flavor. The entire process requires 3-8 months. At the end of this time blackish-brown pods result. Each pod weighs about five grams and is 7-9 inches long and about a quarter of an inch thick. The pods are filled with tiny black vanilla seeds. The entire process from planting to market can take as long as five years.

2. The major component in vanilla extract is a compound called vanillin, $C_8H_8O_3$, but the complete extract contains four major compounds and nearly three hundred minor chemicals.

3. "Imitation vanilla" consists mainly of vanillin that has been synthesized rather than obtained from the vanilla plant, a process that was discovered by German chemists in the 1880s. "Natural" vanilla consists of vanilla that comes from other food sources mixed with a little pure extract. True vanilla extract is obtained from the vanilla plant.

4. Ethyl vanillin is a compound in which the methyl (CH_3-) side chain in a normal vanillin molecule is replaced by an ethyl (C_2H_5-) group. Ethyl vanillin has a vanilla taste that is about three times stronger than that of normal vanillin, but it is insoluble in butter, caramel and chocolate. Consequently, it is found in products like perfumes and low-fat ice cream.

5. Vanilla is a precursor chemical in the manufacturer of medications used to treat Parkinson's disease and high blood pressure. The vanilla-like scent of heliotropin, strongest in Tahitian vanilla, has been found to produce a 63% reduction in patient anxiety during MRI scans. Vanilla is one of the most often used flavorings to mask the bad taste of some medicines.

Teeth Whitening

1. The outermost layer of a human tooth is the enamel. It consists of a translucent layer of calcium phosphate, $Ca_3(PO_4)_2$, and is the hardest tissue in the human body. Just beneath the enamel is the dentin, which determines the color of the tooth. Dentin is made of an off-white matrix of amorphous calcium phosphate and collagen that surrounds the blood vessels and nerves that nourish your teeth.

2. Most discoloration occurs on the surface of the tooth enamel. Modern "whitening" toothpastes rely on abrasive materials such as silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3), to remove these kinds of stains.

3. Most whitening gels rely on hydrogen peroxide, H_2O_2, to remove discoloration that occurs below the surface of the enamel. The peroxide in the gels diffuses through the enamel and into the dentin. There it breaks down into water and oxygen gas via radical intermediates. These radical intermediates contain at least one unpaired electron and are very reactive. It is thought that they react with the pigments that are causing the stain, breaking the pigments down and destroying their color.

4. One method just uses products that can be purchased over-the-counter. These products typically contain adhesive plastic strips that contain a gel of carbamide peroxide and are applied to the front teeth for one half hour twice a day for two weeks. The carbamide peroxide breaks down into urea and hydrogen peroxide, which does the cleaning. Two

other methods are both dentist-supervised. In one the dentist creates a guard tray that fits your teeth. You place a peroxide containing gel in the tray and wear it for the next two weeks whenever you are sleeping. The other procedure occurs strictly in the dentist's office and requires a few visits. Once again, a customized tray is used, but it contains 35% H_2O_2, which is much more concentrated than the peroxide used in the other procedures, so extra precaution is taken to insure that the peroxide only makes contact with your teeth. The decomposition of the hydrogen peroxide is hastened by the use of catalysts and possibly heat or light.

5. Hydrogen peroxide can act as an oxidizing agent by gaining electrons, as the following equation illustrates.

   $2H^+ + H_2O_2 + 2e^- \text{----->} 2H_2O$

   It can also lose electrons and function as a reducing agent:

   $H_2O_2 \text{----->} O_2 + 2H^+ + 2e^-$

Hydrothermal Vents and Giant Tubeworms

1. A hydrothermal vent is an undersea geyser. Very hot mineral laden water shoots out from an opening in the ocean floor. When this hot water meets the cold ocean water, the minerals quickly precipitate out. Many of these minerals are dark in color, so the resulting plume looks like black smoke—thus the name "black smoker."

2. The boiling point of water depends on the external pressure. As the pressure increases, the boiling point of the water increases. The pressure at the bottom of the ocean is so high that the boiling point of the water emerging from a hydrothermal vent can be well above 300 ^oC.

3. The quantity of life that exists around hydrothermal vents is just too great to be living from falling debris. There is no way that there could be enough of this debris to support so much life, and since photosynthesis cannot be taking place there had to be some other way that these organisms were obtaining food.

4. Tubeworms had no mouth, stomach, intestines or any other evidence of a digestive system. Without a digestive system, they could not be feeding on falling debris or other organisms that fed on debris. Furthermore, tubeworms contained an organ called a trophosome, which takes up most of the space in their bodies. Within the trophosome yellow specks of elemental sulfur were found, and biopsies of the organ revealed tubeworm cells filled with clusters of bacteria.

5. The bacteria utilize hydrogen sulfide, H_2S, that is emitted from a hydrothermal vent along with water, carbon dioxide and oxygen that are dissolved in ocean water. In a process that parallels the equation for photosynthesis ($6CO_2 + 6H_2O \text{----->} C_6H_{12}O_6 + 6O_2$), the bacteria utilize H_2S, H_2O, CO_2 and O_2, as illustrated by the following equation (unbalanced):

   $CO_2 + H_2O + H_2S + O_2 \text{----->} [CH_2O]_n + H_2SO_4$

The Mystery of The Pockmarked Paint Job

1. Secondary electrons are electrons produced in a scanning electron microscope when the electron beam created by the instrument ionizes atoms in the sample it is scanning. The higher energy electron beam knocks electrons out of atoms on the surface of the sample.

2. As the electron beam scans the object, the secondary electrons emitted are detected. Areas of greater ionization appear brighter than areas with lower ionization. This variation in the emitted secondary electrons can then be converted into a visual image to produce a photograph of the specimen.

3. When a secondary electron is removed from an atom in a specimen being studied in a scanning electron microscope, it is usually removed from a lower energy level. To fill this vacancy, an electron from a higher energy level will “fall” back to this lower energy level. When this happens X-rays are typically emitted.

4. X-rays have characteristic energies that are unique to the element from which they originated. Thus by studying the energies of the X-rays emitted from a sample in a scanning electron microscope the identity of the atoms in the sample can be determined.

5. Backscattered electrons are the electrons produced when the electrons from the beam inside a scanning electron microscope strike the surface of the sample.

6. The most important information provided by backscattered electrons is the identity of the element being bombarded. Elements with higher atomic number will show up brighter on the computer screen.

Content Reading Materials

National Science Education Content Standard Addressed As a result of activities in grades 9-12, all students should develop understanding	**Vanilla**	**Teeth Whitening**	**Hydro-thermal Vents**	**Chemistry Jobs**	**The Mystery of… (SEM)**
Science as Inquiry Standard A: about scientific inquiry.	✔	✔	✔	✔	✔
Physical Science Standard B: of the structure of atoms.	✔				✔
Physical Science Standard B: of the structure and properties of matter.	✔	✔	✔	✔	✔
Physical Science Standard B: of chemical reactions.	✔	✔	✔	✔	
Physical Science Standard B: of interactions of energy and matter.			✔		✔
Life Science Standard C: of the cell.			✔		
Life Science Standard C: of the molecular basis of heredity	✔				
Life Science Standard C: of the interdependence of organisms.			✔		
Life Science Standard C: of matter, energy, and organization in living systems.	✔	✔	✔		
Life Science Standard C: of the behavior of organisms.			✔		
Earth and Space Standard D: of geochemical cycles.			✔		
Science and Technology Standard E: about science and technology.	✔	✔	✔	✔	✔
Science in Personal and Social Perspectives Standard F: of personal and community health.		✔		✔	
Science in Personal and Social Perspectives Standard F: of environmental quality.		✔		✔	✔
Science in Personal and Social Perspectives Standard F: of natural and human-induced hazards.		✔		✔	

National Science Education Content Standard Addressed (con't) As a result of activities in grades 9-12, all students should develop understanding	**Vanilla**	**Teeth Whitening**	**Hydro-thermal Vents**	**Chemistry Jobs**	**The Mystery of… (SEM)**
Science in Personal and Social Perspectives Standard F: of science and technology in local, national, and global challenges.			✔	✔	✔
History and Nature of Science Standard G: of science as a human endeavor.	✔		✔	✔	✔
History and Nature of Science Standard G: of the nature of scientific knowledge.	✔	✔	✔	✔	✔
History and Nature of Science Standard G: of historical perspectives.	✔	✔	✔	✔	

Anticipation Guides

help engage students by activating prior knowledge and stimulating student interest. If you have time, discuss their responses to each statement before reading each article. Students should read each selection and look for evidence supporting or refuting their responses. Evaluate student learning by reviewing the anticipation guides after student reading.

Directions for all Anticipation Guides: In the first column, write "A" or "D" indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. Cite information from the article that supports or refutes your original ideas.

Vanilla! It's Everywhere!

Me	Text	Statement
		1. Vanilla was discovered originally in Mexican orchids.
		2. People around the world want more vanilla than can be naturally supplied.
		3. There is a chemical difference between natural and imitation vanilla.
		4. The vanilla orchid carries out photosynthesis the same way that other plants carry out photosynthesis.
		5. Vanilla scents are used to reduce patient anxiety during MRI scans.

Teeth Whitening

Me	Text	Statement
		1. Tooth enamel consists mainly of calcium carbonate, $CaCO_3$.
		2. Hydrogen peroxide has been used since the 1800s to whiten teeth.
		3. Hydrogen peroxide can act as both an oxidizing agent and a reducing agent.
		4. Hydrogen peroxide is sometimes used as a rocket fuel.
		5. Once your teeth have been bleached, you probably won't need further bleaching treatments.
		6. Teeth stains caused by the antibiotic tetracycline are permanent.
		7. Teeth actually become more yellow as people age.

Four Cool Chemistry Jobs

To engage students before reading this article, list each job on the board or overhead projector, and ask students to brainstorm how chemistry is involved in each job. The jobs are:

- Science Writer
- Forensic Chemist
- Cosmetics Chemist
- Food Chemist

Then, as they read the articles, then can check to see how many of their ideas were mentioned in the article. They should also list chemical connections they missed. Remind students that just because some of their ideas might not have been mentioned in the article does not mean their ideas are wrong. Perhaps their ideas will be incorporated into products and processes in the future!

Hydrothermal Vents and Giant Tubeworms

Me	Text	Statement
		1. Hydrothermal vents on the bottom of the ocean spew water hot enough to melt the submersible *Alvin*.
		2. The water from the hydrothermal vents is constantly boiling because of the high temperatures.
		3. The hydrothermal vents in the Atlantic and Pacific Oceans are very similar in structure.
		4. The hydrothermal vents can rust if there is no fresh supply of precipitating minerals.
		5. The animals living in hydrothermal vents feed on scraps of food and waste material falling on them.
		6. The tubeworms living in the hydrothermal vents have a complex digestive system so that they can use sulfur compounds.
		7. Dissolved oxygen is abundant in the deep ocean where hydrothermal vents are found.

The Mystery of The Pockmarked Paint Job

Me	Text	Statement
		1. Large chemical manufacturers usually send problems requiring the use of microscopes to biological companies.
		2. Scanning Electron Microscopes (SEMs) form images by using electromagnets to bend beams of electrons.
		3. SEM technology can detect elements at levels far less than 0.1 atomic percent.
		4. Elements with higher atomic numbers appear dimmer on a SEM computer screen.
		5. Underarm deodorants contain compounds of aluminum, silicon, chlorine, and zirconium.

Reading Strategies

These content frames and organizers are provided to help students locate and analyze information from the articles. Student understanding will be enhanced when they explore and evaluate the information themselves, with input from the teacher if students are struggling. If you use these reading strategies to evaluate student performance, you may want to develop a grading rubric such as the one below.

Score	Description	Evidence
4	Excellent	Complete; details provided; demonstrates deep understanding.
3	Good	Complete; few details provided; demonstrates some understanding.
2	Fair	Incomplete; few details provided; some misconceptions evident.
1	Poor	Very incomplete; no details provided; many misconceptions evident.
0	Not acceptable	So incomplete that no judgment can be made about student understanding

Four Cool Chemistry Jobs

One way for students to learn more about these jobs is to *jigsaw*; students are divided into groups to read about and discuss one of the four jobs. Then students go to *home groups* to report on what they found out about the job they discussed. Students should be sure to find out the education requirements for each job.

Alternatively, you may want to provide this organizer to help students locate information about each job.

Job	**Activities of a typical day or week**	**Interesting aspects of the job**	**Education required**
Science Writer			
Forensic Chemist			
Cosmetics Chemist			
Food Chemist			

The Mystery of The Pockmarked Paint Job

<table>
<tr><td colspan="2">Problem:</td></tr>
<tr><td colspan="2">Scanning Electron Microscope (SEM)</td></tr>
<tr><td rowspan="4">How SEM solved the mystery</td><td>How it works:</td></tr>
<tr><td>Secondary electrons:</td></tr>
<tr><td>X–rays:</td></tr>
<tr><td>Backscattered electrons:</td></tr>
<tr><td colspan="2">Solution:</td></tr>
</table>

Hydrothermal Vents and Giant Tubeworms

	Hydrothermal Vents	**Giant Tubeworms**
Location		
Structure		
Interesting Facts		

Also, compare photosynthesis and chemosynthesis in the chart below. (It is like a Venn diagram, but in chart form.)

Photosynthesis	**Chemosynthesis**
Similarities	

Vanilla! It's Everywhere!

Compare natural and synthetic vanilla in the chart below. Remember to include uses!

Natural Vanilla	**Synthetic Vanilla**
Similarities	

Teeth Whitening

Causes of discoloration	**Polishing Agents**
How H_2O_2 is used	**How H_2O_2 works**

Teeth Whitening

Vanilla! It's Everywhere!

Background Information

More on the history of vanilla

The article points out that the first known use of vanilla can be traced back to the Totonaco Indians of Mexico. They were defeated by the Azetcs, who demanded that they turn over this valuable fruit of the Tlilxochitl vine. The Aztecs, in turn, were conquered by Hernando Cortez around 1520. Bernal Diaz, a Spanish officer under Cortez, may have been the first white man to take note of vanilla when he observed the Aztec emperor Montezuma drinking "chocolatl." It is generally assumed that Montezuma introduced Cortez to this highly valued beverage.

It is thought that the plant was taken to England some time before 1733, but evidently was lost. It wasn't reintroduced until the beginning of the 19^{th} century. There is a record of it flowering in the garden of Charles Greville in 1807. Cuttings from this garden were taken to botanic gardens in both Paris and Antwerp. In 1819 two plants were sent to Buitenzorg, Java. One didn't survive the journey. The other flowered in 1825, but did not bear fruit. Additional plants were taken to several other locations around the world.

Although it turned out that the plants could be grown successfully in tropical climates, they failed to produce fruit, which was the goal of transporting and cultivating them. As pointed out in the article, effective pollination required the presence of Mexican Melipona bees. As a consequence, Mexico served as the only real source of vanilla for several years.

Then in 1836, a man named Charles Morren discovered that the flowers could be artificially pollinated, and five years later a former slave developed a practical method of achieving this by use of a sharp bamboo stick—the method that is still used today.

Cultivation and processing of vanilla plants

Commercial vanilla plants are always cultivated from stem cuttings. It takes between 3-4 years for the cuttings to flower and fruit. The plants grow best in humid tropical areas that have abundant rainfall. The vines are grown on supporting poles usually about three meters apart. The orchid itself blooms only one day a year. Since bees cannot be counted upon to pollinate all the orchids on the days that they bloom, artificial pollination using bamboos sticks is always utilized. A period of about 6-9 months separates flowering from harvesting. Picking the pods at precisely the correct time is critical. If picked too early the resulting vanilla will be of inferior quality. If picked too late, the pods will split during the curing process.

A nice Website for photographs of various vanilla plants is:

http://www-ang.kfunigraz.ac.at/~katzer/engl/generic_frame.html?Vani_pla.html

When first picked, the pods are green in color. They do not have the characteristic smell or taste of vanilla. Those develop when the pods are cured. To cure, the pods are immersed in boiling water for about 20 seconds. They are then wrapped in blankets. Each day they are left in the sun to dry and brought in to sweat each night. This results in their shrinking and their color changing to a dark brown. This process is very labor intensive, which accounts, in part, for the high cost of true vanilla extract obtained this way.

Some interesting facts about vanilla

The flower of the vanilla plant, *vanilla planifolia*, is a member of the orchid family. There are somewhere around 25,000-30,000 different species of orchids and an estimated 100,000 different hybrids. The fruit of the vanilla plant is the only species of orchid fruit that is edible!

There are two other species that can be cultivated, but are generally considered to be of inferior quality, *Vanilla pompona* and *Vanilla tahitensis*.

For centuries vanilla was always used in conjunction with cacao beans to make the “chocolatl” beverage discussed in the article. Cortez was offered the drink by Montezuma. For some reason no one thought of utilizing it as a stand-alone flavoring until 1602, when Hugh Morgan, one of Queen Elizabeth I’s apothecaries, made the suggestion.

The United States is the largest importer of vanilla, followed by France and then West Germany.

Different types of vanilla

There are several different types of vanilla, depending on the specific species of plant from which it originates as well as the geographical location where it was grown and its form or grade. Three major types are:

Madagascar Bourbon Vanilla Beans

These originate from the island of Madagascar and the West Indian island of Reunion. Madagascar beans account for about three-fourths of the world’s supply of vanilla.

Mexican Vanilla Beans

These come in a variety of grades. Considered to be of high quality at one time, much of the crop was destroyed by a devastating freeze about forty years ago. Some still remain of high quality, but are scarce. Many of the original fields have been converted to either oil fields or orange groves.

Tahitian Vanilla Beans

Although highly aromatic, often suggestive of the odor of licorice, cherry, prunes or wine, these beans are not considered to be as flavorful.

Thomas Jefferson and Vanilla

The sidebar to the article mentions that Thomas Jefferson brought vanilla to the United States. He actually had a recipe for vanilla ice cream. A bit difficult to read (why didn’t he just use a word processor?), it appears on the next page.

Ice cream.

2 bottles of good cream.
6. yolks of eggs.
½ lb sugar
mix the yolks & sugar
put the cream on a fire in a casse-
-role, first putting in a stick of Vanilla.
when near boiling take it off &
pour it gently into the mixture
of eggs & sugar.
stir it well.
put it on the fire again stirring
it thoroughly with a spoon to
prevent it's sticking to the casse-
-role.
when near boiling take it off and
strain it thro' a towel.
put it in the Sabottiere.
then set it in ice an hour before
it is to be served. put into the
ice a handful of salt.
put ice all round the Sabotiere.
i.e. a layer of ice a layer of salt
for three layers.
put salt on the coverlid of the
Sabotiere & cover the whole with
ice.
leave it still half a quarter of an
hour.
then turn the Sabotiere in the
ice 10 minutes
open it to loosen with a spatula
the ice from the inner sides of
the Sabotiere.
shut it & replace it in the ice
open it from time to time to de-
-tach the ice from the sides.
when well taken (prise) stir it
well with the Spatula.
put it in moulds, justling it
well down on the knee.
then put the mould into the
same bucket of ice,
leave it there to the moment
of serving it.
to withdraw it, immerse the
mould in warm water,
turning it well till it
will come out & turn it
into a plate.

How genuine vanilla extract is distinguished from artificial vanilla

The chief flavoring agent in genuine vanilla extract is vanillin. Genuine vanilla extract is made from the harvested beans of the vanilla orchid. Although the harvested beans contain very little vanillin, the compound is produced as the beans ferment, along with hundreds of other compounds.

In the 1950s it was discovered that synthetic vanillin could be made from a waste product of the wood pulp industry. Thus it became possible to make artificial vanilla very inexpensively.

This, of course, creates the potential for fraud. The preparation of pure vanilla extract requires a great deal of time and is very labor intensive, requiring perhaps 3-6 months of curing to develop the full flavor. Artificial vanilla can be made cheaply. It still contains vanillin, but does not contain the complexity of other chemicals contained in true vanilla extract.

As pointed out in the article, vanilla is the only flavoring to have an FDA standard of identity. Pure vanilla extract must contain, "the extractive material from 13.35 oz. of vanilla beans per gallon and at least 35% alcohol by volume."

But can we tell the difference?—see *Demonstrations and Lessons*.

Well, whether we can tell or care about the difference of course isn't the point. The FDA mandates that any product sold as vanilla extract must, in fact, be vanilla extract.

A somewhat nonscientific comparison of different types of vanilla

In most of the purchasing decisions we make every day, we need to choose between various "qualities" that are available for a given type of product. Sometimes the quality difference is fairly discernible, but in the vast majority of cases coming to an accurate determination of the real difference in quality is not easily accomplished. Furthermore, there is always the question of whether some perceived or real quality difference is worth the additional cost. *Consumers Reports* and similar magazines are devoted to trying to make such determinations.

Vanilla provides us with a simple but illustrative example that ties nicely into chemistry.

I went to a local supermarket and purchased two bottles of "vanilla." One was labeled "Imitation Vanilla." It cost $2.99 for 8 fluid ounces. The label indicated that the ingredients were:

water, propylene glycol, caramel color, ethyl vanillin, artificial flavors, vanillin

A bottle of "Pure Vanilla Extract" with no country of origin listed cost $2.99 for 2 fluid ounces. It contained:

vanilla bean extractives in water, alcohol (35%), and corn syrup

Mrs. Cardulla enjoys gourmet cooking for a hobby, so naturally she had purchased genuine Madagascar Bourbon vanilla. An 8 fluid ounce bottle, purchased some time ago, cost $18.00, and when recently replenished, the cost had risen to $29.00. The label on the bottle was interesting. It what might be judged an effort to validate the price in the eyes of the consumer, it provided a nice, fairly accurate history of vanilla along with some information, also accurate, about what goes into making genuine Madagascar vanilla extract.

> *Vanilla, the most popular flavor in the world, originated in Mexico. Brought to Europe about 1520 by the explorer Cortez* (it is interesting to note that on the label Cortez is an "explorer," but not a conqueror). *It was first used only in conjunction with cacao beans in a drink called Chocolatl. Since 1602 it has been enjoyed as a flavor by itself.*

Grown mainly in Madagascar and Indonesia as well as other minor areas, the vanilla bean, or pod, is the only edible fruit-bearing orchid. Each flower, open only one day a year, must be hand pollinated to produce a pod which requires a labor intensive 3-6 month curing process to develop full flavor. About 5 pounds of harvested pods produce only 1 pound of cured pods.

Our exclusive cold process method extracts the essence from selected vanilla pods, the finest obtainable, producing rich and delicious flavor that is unsurpassed. USE AND ENJOY!

The contents read:

Water, alcohol, sugar, vanilla bean extractives

The product is legitimate. The differences between the various "qualities" are real and obvious from the labels. The Madagascar vanilla contains no corn syrup, no added colorings, propylene glycol, ethyl vanillin, artificial flavors or vanillin manufactured rather than obtained from plants.

But can one really tell the difference if the labels were removed?

There are really two questions, (1) can we discern any difference, and (2) which product would we prefer if we couldn't see the labels?

First an aroma test was conducted. The three different vanillas were placed in identical very small glasses. A deck of cards containing only three suits was shuffled. Each suit corresponded to a different vanilla. Turning over the top card would determine which vanilla was going to be blind tested. Reshuffling and repeating would randomize the choices so no experimental bias could enter into the order in which the vanillas were given to the person sampling them.

The test was performed rather superficially; just to get a rough idea whether any differences would be discernible at all.

And the results were…

Classified, so as to not bias any experiments done in class or as student projects.

Then a grande half-skim latte was purchased at a local coffee shop. Again it was evenly divided into three cups. Each cup was lined up with one of the vanillas and one-half ounce of that vanilla added to the cup.

My wife volunteered to be the taster. First she sampled each latte to see if she thought there was any difference. She indicated that yes, she could taste a difference, especially between the latte flavored with the imitation vanilla and that with the Madagascar vanilla. But was this perceived difference influenced by the fact that she knew which vanilla she was tasting and had indicated that she would never prepare something using anything other than genuine Madagascar Bourbon Vanilla Extract?

Then the blind taste test took place. Once again randomizing the order, she tasted each latte and indicated which vanilla she thought it contained and which she preferred.

Once again, the results are "classified," but are revealed at the end of the "funny story" at the end of the Teacher's Guide material.

A similar experiment might make for an interesting and "fun" class experiment, either in class or as a group project. Of course care much be taken in regard to consuming food products in a laboratory setting. See *Demonstrations and Lessons* and *Suggestions for Student Projects.*

A blind taste test done by *Cook's Illustrated* magazine

Just as this Teacher's Guide was going to press, the November-December issue of *Cook's Illustrated* magazine came out with a blind taste test comparing imitation vanilla to both inexpensive and premium vanilla extracts. They used them to prepare both plain yellow butter cake and crème anglaise, a simple vanilla-flavored custard sauce. The tasters included both pastry chefs and baking experts.

Similar tests were done in 1995 and repeated after that. Every time the test produced the same results. The tasters had great difficulty in discerning any difference between products made with imitation vanilla versus products that were prepared with premium vanilla extract. The results were the same this year as well. All vanillas were basically indistinguishable, especially in the cake. Although slight distinctions were made for the custard sauces, when the tasters were pressed, many expressed a preference for the imitation vanilla, describing it as being "stronger and easier to detect."

As Mark Twain once wrote, "You pays your money, and you takes your choice."

Connections to Chemistry Concepts

Some organic structures were presented in the article. If it would be beneficial to access a Website for information on the naming of organic compounds, a few good ones can be found at:

http://www.angelfire.com/bc2/OrgChem/

http://www.acdlabs.com/iupac/nomenclature/

http://www.chem.ucalgary.ca/courses/351/Carey5th/nomenclature/

Possible Student Misconceptions

There are a number of misconceptions that students or anyone else might have about vanilla if they've never read or heard much about the product. The article does a very nice job of addressing these possible misconceptions. There also are some unexpected facts about vanilla that most people would probably not believe would be true, but are. It might be interesting to test students about these misconceptions and facts before and after they read the article. The following might even make for a fun true-false quiz. True or false?--

Vanilla is vanilla. There really isn't any difference between expensive and less expensive brands.
It doesn't matter which country vanilla comes from. All vanilla is considered to be of identical quality.
Vanilla comes from an orchid plant. It is the only orchid plant that produces an edible fruit.
Vanilla is a more popular flavoring than chocolate.
Vanilla is and was considered to be an aphrodisiac by many people.
Most chocolate recipes call for vanilla.
Vanilla is used to flavor cattle food and tobacco.
High quality vanilla is grown in the United States.
The flower of the vanilla plant opens for only one day.
Vanilla plants can be easily grown in greenhouses.
Natural vanilla is made up almost entirely of a pure compound called vanillin. Artificial vanilla is a mixture of several compounds.
Vanilla is the only flavoring to have an FDA specified standard of identity.

Vanillin, the major compound in natural vanilla, can be made from petroleum, wood pulp, and coal tar.
Vanilla can be used as an insect repellent or put on fly paper to attract flies.

Demonstrations and Lessons

1. Given the variety of vanilla products on the market and the rather significant variation in their costs, it might be interesting to design and conduct a controlled experiment to determine whether most people can in fact discern any difference between the products, and if so, which they actually prefer. See *Background Information* and *Suggestions for Student Projects.*

2. Companies that sell vanilla and vanilla related products often make what may sound like somewhat exaggerated claims about the properties, uses and virtues of vanilla. But some of these claims may, in fact, be rooted in long-known qualities. Designing and carrying out appropriate experiments to test some of these claims could make for an excellent laboratory activity. See *Suggestions for Student Projects*.

3. Artificial vanilla can be manufactured much more cheaply than true vanilla extract can be produced (see *Background Information*). But can the average consumer tell the difference, and if so, would they prefer true vanilla extract if they didn't know which was which? Your local supermarket probably sells at least a few different brands and types of vanilla, from "imitation vanilla," to vanilla extract that is not made from vanilla planifolia. They may also carry what is generally considered to be the best quality vanilla—Madagascar Bourbon vanilla extract.

   It might be interesting to conduct a "blind taste test" to try and answer this question. The activity contained in the article provides one way of doing this. But if you don't care to go through all the steps required to actually prepare a vanilla cream sauce, a simpler procedure might be utilized. First students might test the aroma of several beakers labeled simply "A," B,","C," "D", etc. some of which hold different qualities and types of vanilla extract and some that hold artificial, or imitation vanilla. Can they discern any difference at all—even if they can't state which is which? They could then place a small amount of the "pure" vanilla on their tongues and see again if they can discern any difference, if they have a preference, and if so, for which product.

   They could perform a taste test by adding the different types of vanilla to something like coffee or some other suitable beverage.

   My wife and I did a relatively simple experiment along these lines—see *Background Information*.

Connections to the Chemistry Curriculum

While there aren't a large number of chemistry connections in this article, it can lead to a discussion of organic structures, functional groups and nomenclature. If the "blind taste test" is done either as a class experiment or as a student project, this should tie nicely into the notion of designing an appropriately controlled experiment with a suitable sample size and perhaps even to a discussion of how statistically reliable the results of a given experiment are.

Suggestions for Student Projects

1. There are large number of companies that sell vanilla and vanilla related products. As might be suspected, some of them make somewhat dramatic and perhaps unusual claims about the virtues of vanilla. The following were found on some Websites:

Vanilla is an antacid—a “few drops” added to pineapple, fruit salads or sauces containing citrus will “soften” the sharpness. Put a little in tomato sauce and it will “neutralize the acidity.”

It can neutralize the bite of hot peppers. It will “soften the bite but bring out the sweetness and flavor of the peppers.”

It will keep spiders off of your furniture. Add a vanilla bean or two to you furniture polish. Apply to both sides of your furniture. The claim is made that “Bugs don’t like the smell and will leave.”

It will cut the smell of house paint. Add a tablespoon of vanilla extract to a gallon of paint and it will cut the smell.

True, or bogus claims? A group of students could design experiments to test some or all of these claims. How will be effectiveness be determined? What kind of controls are needed? They could do the experiments and report back to the class.

2. If you believe that knowledge of geography represents a worthwhile goal for our students, this article certainly presents an opportunity to have students who share this interest to pursue a connected project. If you investigate both the history of the cultivation of vanilla beans as well as the current sources of several types, you quickly encounter geographical locations with names such as Madgascar, Mexico, Guadeloupe, Tahiti, Indonesia, Java, Paris, Antwerp, Reunion, Coromos Islands, Guatemala, Bay of Campeche, Boco-toro, Costa-Rica, Antilles and many others. It would be a challenge for a student or group of students to research the history of vanilla and the various current sources of the bean and then prepare a world map locating and marking each of the locations they found a reference to.

3. **Taste Test:** Compare sauces made from vanilla bean, vanilla extract and imitation vanilla. Make the following recipe three times, using three types of vanilla flavoring. You could cook up the sauces in the lab if it is approved for food chemistry, or at home or in the school kitchens. Have several volunteers do a blind tasting of each cooled sample, (use a clean plastic spoon for each taste) and rate each for vanilla flavor and aroma. The tasters should not see what they are testing, because the tiny seeds or a difference in color might influence taste. Use a rating of 5 (for most vanilla flavor) to 1 (for least.)

Vanilla Cream Sauce

2 egg yolks
20g sugar
200 ml whipping cream
100 ml milk
½ vanilla bean OR 10 ml pure vanilla extract OR 10 ml imitation vanilla
(Slit the bean open carefully, to release the seeds. Put both seeds and pod into the sauce. Hint: if the bean is too hard to cut, soak it in the measured milk for an hour.)
100 ml whipping cream
3 plastic spoons for each taster

Mix the first five ingredients together over low heat. Stir continuously until the sauce thickens. Let cool. Whip the remaining cream and fold it into the sauce. Remove all pieces of vanilla pod. Any sauce left over from the testing will be good with bananas or whatever fruit is available.

Surprised at the result? Or not? Think like a chemist. Extracting all the flavor from a bean can take weeks, in alcohol. Pure extract contains more flavor chemicals than imitation, but imitation may contain a higher concentration of vanillin. So which type of vanilla delivers the most flavor to your sauce? You be the judge. It comes down to personal choice. And price.

Anticipating Student Questions

1. Could I grow vanilla at home?

   Not unless you live within about 10-20 degrees north or south of the Equator. It can be grown in Puerto Rico, South Florida and Hawaii, but not as successfully as in Madagascar or some areas of Mexico. It is possible to grown vanilla in greenhouses, but the plants often do not flower or fruit. It really is quite difficult to grow successful vanilla plants, which certainly contributes to the relative high cost of the “real thing.”

2. Does Madagascar Bourbon vanilla actually contain Bourbon?

   No. The name is derived from the historical period when the island of Reunion was ruled by the Bourbon kings of France. Although there is alcohol in Madagascar vanilla extract, it is simply normal ethanol, not Bourbon whiskey.

3. Why is there so much alcohol in genuine vanilla extract?

   Because alcohol happens to be the most efficient agent for extracting the flavor from the beans. When vanilla extract is used in cooking or baking this alcohol will evaporate away.

4. How long can you keep vanilla extract before it is no longer good.

   That depends on how it is stored. Vanilla extract comes in brown bottles, which protect it from light. It really should be stored away from light and heat, but not in a refrigerator. If kept in a pantry away from any heat sources, the quality should remain good for several years.

Web Sites for Additional Information and Ideas

An excellent general Website for information on just about anything relating to vanilla is:

www.shanks.com/vanilla

It contains links to information about the history of vanilla, major types of vanilla, the botanical nature of vanilla, its ecology, its cultivation, its processing and manufacturing as well as spoilage.

Another “funny story”

While doing the small “blind taste test” described in *Background Information*, my wife and I engaged in a discussion as to whether pure Madagascar Bourbon Vanilla Extract was really worth the extra cost. I asked my wife whether she really thought that she would be able to tell the difference between some product made with cheap imitation vanilla or the “real thing.” She replied, with a tone that moved from adamant to quiet:

I KNOW I COULD TELL THE DIFFERENCE…probably…maybe…I think

At another point she stated that she would never use imitation vanilla because she didn’t want to cook with something “that contained a lot of chemicals.”

She was able to identify each of the three vanillas added to some café latte with high accuracy (only one error in twelve trials), and indicated a definite preference for the latte that was flavored with the Madagascar Vanilla.

Teeth Whitening

Background Information

More on the History of Teeth Whitening Agents and Toothpaste

There is evidence that attempts to whiten teeth may date back several thousands of years. That is probably not surprising. While what is considered to be physically attractive certainly varies widely from culture to culture and from one historical period to another, a complete set of evenly spaced, well formed and white teeth does appear to have been considered a positive asset for much of recorded history.

The first recorded attempts to prepare what might loosely be called a toothpaste may date as far back as 5000 BC, when ancient Egyptians prepared a mixture consisting of the powdered ashes of animal's hooves, myrrh, powdered and burned eggshells and pumice. It isn't too difficult to imagine what that type of mixture might have been like. Myrrh is a yellowish brown to reddish brown aromatic rum resin obtained from a tree. It is said to have a bitter, slightly pungent taste. Mix in the other gritty, abrasive ingredients and it seems reasonable that such a concoction might be successful at whitening teeth, although it would appear only at the sacrifice of the tooth enamel itself.

The Greeks and Romans attempted to improve the taste of this type of mixture, but other than that, there doesn't appear to have been any significant improvements to this much less than ideal product until perhaps about 1000 AD. The Persians recommended that somewhat less harsh abrasives, such as the burnt shells of snails and oysters be used and their recipes included materials such as herbs and honey.

A more comprehensive list of the kinds of things that were used in ancient versions of toothpaste is both interesting and at times, perhaps repulsive. Included are:

Burnt hartshorn—the hart is a male deer, commonly the red deer. Hartshorn refers to the antler of a hart. It is a source of ammonia.
Burned gypsum
Dried animal parts
Various minerals
Green lead
Verdigris (see *ChemMatters*, Feb. 2003)
Incense
Powdered flintstone
Powdered fruit
Talc
Dried flowers
Mice
Lizard livers
Urine
Salt

The toothpick preceded the toothbrush. The first "toothbrushes," really didn't contain any brushes, but rather were what amounted to toothpicks covered with cloth. The bristle toothbrush originated in China just prior to 1500 and was introduced in Europe during the 1600s.

By the late 1700s a version of what might be called a somewhat modern toothpowder became available in England. It consisted of a highly abrasive mixture of brick dust, china, earthenware or cuttlefish. Glycerine was added to improve the taste and later Borax powder was used to produce foam. Soap was added in 1830 and chalk in 1850. In 1892 the first collapsible tube was used to hold toothpaste and was marketed by Dr. Washington Sheffield as "Dr. Sheffield's Crème

Dentifrice." Four years later Colgate Dental Cream became the first toothpaste to achieve widespread distribution in such tubes.

A toothbrush timeline

~3000 BC—Egyptians gnaw on "chew sticks" after a meal. These consist of sticks whose ends have been frayed into soft fibers. Numerous examples of this type of stick have been found in Egyptian tombs.

~500 BC—Some Romans employ slaves to clean their teeth.

1498—The first toothbrush that actually is a brush is invented in China. It uses hairs from the neck of a boar that are attached to bamboo or bone handles.

1600s—Toothbrushes are brought to Europe by travelers that have been in China.

1780—William Addis of Clerkenwald, England develops the first mass-produced toothbrush. It is made by attaching hairs from the tail of a cow to a whittled cow thighbone.

1880—A product called "Dr. Scott's Electric Toothbrush" is marketed, but it really isn't an electric toothbrush at all. The ads simply claim that it is "permanently charged with electromagnetic current." The first real electric toothbrush was created in 1939. The first electric toothbrush isn't marketed in the United States until 1960, under the name Broxodent.

1938—Dr. West's Miracle Tuft Toothbrush makes its debut

1941-1945—American soldiers are ordered to brush their teeth regularly. Amazingly, this really marks the first time that tooth brushing becomes a normal part of American daily routine.

1950—The first soft nylon bristle toothbrush is invented. It is much less irritating to tissue.

More about the structure of teeth

The structure and composition of a human tooth is perhaps somewhat more complex than the relatively basic structure and composition presented in the article. The outer enamel is indeed the hardest material found in the human body, as it is for any mammal that has teeth. It is highly mineralized, but not entirely made of calcium phosphate. It consists of about 95-98% inorganic material by mass. About 90-92% of this inorganic matter is a slightly modified form of calcium phosphate called hydroxyapatite. The formula for hydroxyapatite is $Ca_5(PO_4)_3OH$. There are also trace amounts of other minerals. The remainder of the enamel consists of about 1% protein and 4% water by mass. The proteins that are contained in tooth enamel are not found anywhere else in the human body. These proteins are called enamelins and amelogenins.

A couple of good diagrams of tooth structure can be found at:

http://www.tpub.com/dental1/26.htm
http://www1.us.elsevierhealth.com/SIMON/Bird/modern/EIC/graphics/7627_04_24.jpg

The bulk of a tooth is comprised of dentin. Dentin also contains a high percentage of hydroxyapatite, but not as high as enamel--perhaps 67-75%. The organic portion of dentin consists of about 90% collagen and 10% other proteins. Dentin is about 5-10% water by mass.

The outer layer of the root portion of a tooth is made of something called cementum. Cementum is softer than dentin and is comprised of about 45-50% hydroxyapatite and 50-55% water and organic matter made of proteins.

The innermost pulp of a tooth is made mostly of nerves and blood vessels.

Connections to Chemistry Concepts

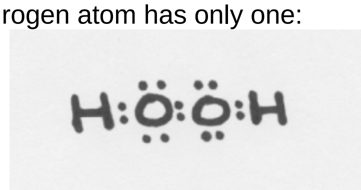
Why urine was used in some old toothpaste formulations

It may seem surprising that one common material used in many old toothpastes was human urine (see *Background Information*), given that most people would probably find brushing their teeth with a material that contained such an ingredient distasteful. This material was used for the same reason that hartshorn was sometimes utilized (see *Background Information*). It is a source of ammonia, and ammonia is a good general-purpose cleaner.

The structure of hydrogen peroxide

The structure of hydrogen peroxide is somewhat more complex than its simple formula might suggest.

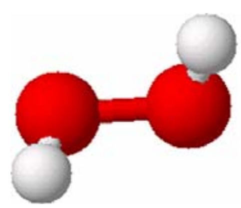
The electron dot (Lewis) structure of H_2O_2 is very straightforward, given that an oxygen atom has six valence electrons while a hydrogen atom has only one:



While the Lewis structure might suggest to students that the structure is linear, VSEPR theory would argue that the four pairs of electrons that surround each oxygen would tend to be directed more or less towards the corners of a tetrahedron. This in turn might suggest bond angles somewhere near the normal tetrahedral angle of 109^o 28'.

But since the two unshared pairs occupy more room than the shared pairs, the actual structure is somewhat more complicated and not immediately obvious. A nice illustration of the experimentally determined structure can be found at

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch10/group6.html



Why hydrogen peroxide can act as either an oxidizing or a reducing agent

The oxidation state of the oxygen atom in hydrogen peroxide is -1. In oxides it is -2, while in free oxygen gas it is 0.

Oxidation occurs when an atom increases its oxidation number (equivalent to losing electrons). Hydrogen peroxide can be oxidized from the -1 oxidation state to the 0 oxidation state, thus functioning as a reducing agent.

$$H_2O_2 \text{ -----> } 2H^+ + O_2 + 2\ e^- \qquad E^o = -0.68 \text{ volt}$$

The moderately negative value for the oxidation potential for H_2O_2 suggests that it can indeed function as a reducing agent, albeit not a particularly strong one.

It can also be reduced from the -1 oxidation state to the -2 oxidation state, thus functioning as an oxidizing agent:

$$H_2O_2 + 2H^+ + 2\ e^- \text{ -----> } 2\ H_2O \qquad E^o = 1.78 \text{ volt}$$

The relatively large value for the reduction potential for H_2O_2 in turn suggests that it would function as a rather strong oxidizing agent.

The decomposition of hydrogen peroxide into water and oxygen gas is an example of a *disproportionation reaction*, sometimes referred to as auto-oxidation-reduction. If the above two half-reactions are added, one obtains:

$$2\ H_2O_2 \text{ -----> } 2H_2O + O_2 \qquad E^o = 1.10 \text{ volt}$$

The positive overall voltage for this reaction indicates that hydrogen peroxide is thermodynamically unstable and will spontaneously decompose into water and oxygen gas. This is the case, but the reaction is not rapid at room temperature, so solutions of hydrogen peroxide can be kept for significant periods of time if stored at cool temperatures in bottles that do not allow light to enter.

But the decomposition can be made to occur very rapidly if an appropriate catalyst is present.

There are a large number of substances that will catalyze the decomposition of hydrogen peroxide. Included among them are:

Blood
Manganese dioxide, MnO_2
Potassium iodide
Potatoes, or any material that contains the enzyme catalase
Human saliva (contains an enzyme called peroxidase)
Several metallic ions, including Fe^{2+}, and Fe^{3+}.

Possible Student Misconceptions

1. Because toothbrushes are very simple-appearing devices and so common, most of our students probably assume that something very similar to the type we use today must have been around for centuries. While the first bristle toothbrush does date back to about the beginning of the 1500s, it wasn't until the invention of nylon in 1937 that the creation of mass-produced toothbrushes at reasonable prices became practical. The first, appearing in 1938, apparently was called Dr. West's Miracle Tuft Toothbrush. You can find images of some of the original advertisements for this product at:
   http://www.yesterdaypaper.com/ad_pages/3052.html
   http://historyproject.ucdavis.edu/imageapp.php?Major=AD&Minor=Y&SlideNum=36.00

   The latter actually utilizes an image of a young woman in a somewhat daring state of undress (by 1940 standards). The price for the brush is $0.50--actually rather expensive for that time.

   Given its apparent simplicity, students will probably be amazed more than 3,000 different patents have been issued for various kinds of toothbrushes.

2. Students may assume that since tooth whitening procedures whiten teeth, they will also whiten caps or fillings. This is not the case, and can be a problem for individuals that have a number of capped teeth because after going through the whitening procedure there can be a difference between the color of their teeth and the color of their caps.

Demonstrations and Lessons

1. There is a famous "Elephant Toothpaste" demonstration that is a remarkable fit to this article. It really doesn't have anything to do with toothpaste, but the title certainly is appropriate, and the demo relies on the decomposition of hydrogen peroxide. The decomposition of a 30% solution of H_2O_2 is catalyzed by a saturated solution of potassium iodide. The basics of the demo are that a large graduated cylinder is about one-fourth filled with a 30% solution of H_2O_2. Some liquid soap is added. Some liquid food colorings are poured down the side of the graduated cylinder to produce the colored stripes that are characteristic of some popular toothpastes. When the solution of KI is poured into the cylinder, the rapid decomposition of the H_2O_2 with the resulting generation of O_2 gas causes the mixture in the cylinder to foam up rapidly and shoot out of the top of the cylinder. The colored stripes are suggestive of the appearance of toothpaste.

   There are a number of Websites that provide detailed directions for performing this demonstration safely and cleanup. A Google search using the phrase "elephant toothpaste" will turn up several. A couple of good ones are:
   http://www.carolina.com/chemistry/experiments/elephant.asp?print=yes
   http://www.thecatalyst.org/download/demos/elephant2.pdf

2. If you teach an honors, AP, or somewhat advanced course, there are a number of good laboratory experiments related to the decomposition of hydrogen peroxide and the role that catalysts play in the decomposition.

   A Google search using phrases such as "hydrogen peroxide" + decomposition + catalysts + experiment should produce something around a thousand "hits." Possible experiments range from the relatively straightforward and simple to some that are rather involved and sophisticated. A few that might be appropriate, depending upon the academic level of the course and the time available include:
   http://www.chemheritage.org/EducationalServices/faces/env/activity/Catalysi.htm
   http://chemed.chem.purdue.edu/demos/moviesheets/19.6.html
   http://www.woodrow.org/teachers/chemistry/institutes/1988/catalyst.htm
   http://chemed.tamu.edu/molvis/Summer_02_Learning_Cycles/TJ_tato_Lab-teacher.pdf

Connections to the Chemistry Curriculum

This article connects strongly to the topic of oxidation-reduction, especially the redox reactions of hydrogen peroxide, and any discussion of hydrogen peroxide will almost certainly bring one to a discussion of catalysts and how they operate. The interesting and perhaps somewhat unexpected structure of hydrogen peroxide will lead to electron dot (Lewis) structures and VSEPR theory. If the article brings you to a discussion of dental health in general, the topic of fluoridation will probably arise, and this ties into a significant amount of information and opinion--scientific, political and philosophical (see *Suggestions for Student Projects*).

Suggestions for Student Projects

1. Like breakfast cereals, the number of different toothpastes there are to choose from is perhaps somewhat amazing. But how different are they? Students might choose to select several popular brands of toothpaste, compare their ingredients, and perhaps contact the various companies, comparing their arguments as to why their particular product is the "best" (one might assume that each would make that claim). They could run a double blind comparison study using classroom volunteers. What is the price variance between expensive "name" brands and generic or less expensive brands? Can they really notice any difference, or are purchases made based upon advertising, habit, or product packaging?

2. There is a wide range of different over-the-counter products designed to whiten teeth. Some claim to the "5 minute" whiteners, while others have directions for applications more

in line with what we might expect. While there are several similar ingredients, the products do vary somewhat in the substances they contain. While it is doubtful that their effectiveness could be compared in a manner similar to what is described in the previous suggested project, students could certainly compare the labels and the claims of competing brands.

3. There are a number of laboratory experiments dealing with the decomposition of hydrogen peroxide and the effects of different catalysts on the rate of decomposition--see *Demonstrations and Lessons*. One or more of these experiments (or others that students can locate on the Web) could be set up and performed by students or small groups of students working together.

4. As discussed in *Background Information* and *Possible Student Misconceptions*, there has been a real evolution in the development of both toothbrushes and toothpastes. The claims made for various products and the advertisements designed to sell them can often reveal a great deal about the cultural values of an era and the role that government played (or didn't play) in protecting consumers. Students with an interest in history might want to research popular advertising from a period like that surrounding WWII or the 1950s or 1960s, reflect on what is suggested of U.S. society by the content and focus of these ads. How are women portrayed? What kinds of personal characteristics and attitudes seem to be valued? What kinds of claims are made for a product? Do these claims seem reasonable?

5. It is entirely possible that one or more of your students or members of their immediate family may be planning to utilize one of the possible teeth whitening procedures mentioned in the article. If this is the case, it could provide a convenient basis for a student project involving determining the effectiveness of the procedure along with any problems that are associated with it. If several different individuals plan to use different types of procedures, then it may be possible to do at least small-scale comparison of the effectiveness of these different procedures.

6. Although not directly connected to the topic of teeth whitening, after more than a half century, the issue of fluoridation of drinking water continues to engender some controversy and often high emotion. As such, it can provide an excellent opportunity for students to investigate this kind of issue--one that connects strongly to science as well as political and philosophical ideas. There clearly is a lot of science relating to the effects of fluoridation. Many studies that have been done in this area, but both proponents and opponents of fluoridation can, of course, find support for their positions. This topic would be an excellent one for students to research, weighing the arguments of both sides and trying to determine their own position on the issue. How does one evaluate the validity of opposing arguments? This topic could result in an outstanding classroom report or debate.

Anticipating Student Questions

1. Is there any way of preventing the staining of teeth due to smoking?

   Yes. Stop smoking. Other than that, there is no way to prevent the staining from smoking or the use of chewing tobacco.

2. Is it true that fluoride in drinking water will stain your teeth?

   Yes and no. It is true that at concentrations higher than 1 ppm fluoride in drinking water can definitely produce stained, or what are referred to as “mottled” teeth. In fact, the discovery that fluoride in drinking water can reduce the incidence of cavities in teeth came about when early in this century it was noted that people who lived around Colorado Springs had a very high incidence of stained or “mottled” teeth, but at the same time had a very low

incidence of dental cavities. Both effects were eventually connected to high concentrationsof fluoride in the local drinking water.
But at concentrations below 1 ppm this staining does not occur to any significant degree.

Web Sites for Additional Information and Ideas

The article states that studies using Scanning Electron Microscopy have shown that the use of teeth whitening agents does not damage tooth enamel. There are a number of studies that came to this conclusion. Two can be found at:
http://www.dentalcare.com/soap/journals/pgresrch/posters/aadr01/pp1391.htm
http://www.discusdental.com/clinical/cdsada1.html

Additional information about carbamide peroxide (urea hydrogen peroxide) can be found at:
http://www.chem-world.com/pdf/Techinfo-UHP.pdf

Four Cool Chemistry Jobs!

The Website of the American Chemical Society is an excellent resource for information about careers in chemistry and chemistry-related fields. In addition there is a wealth of information that should prove interesting and useful for chemistry students even if a career in the field is not on their horizon.

Exploring some of the material and features available at the ACS Website would make an excellent activity—perhaps on one of those days during a school year when for one reason or another (assemblies, shortened periods, student absences, students absent because of an activity or field trip—the list of reasons why "normal days" can often seem like exceptions seems endless at times) trying to conduct a regular classroom session isn't practical.

Students could visit the ACS Website, link and examine some of the features and material that is available. For example, if you go to:

http://www.chemistry.org/portal/a/c/s/1/general.html?DOC=vc2\index.html

you will be at the VC_2, or Virtual Chemistry Club page. From there you can link to pages like:

What's That Stuff?

This will in turn link to a discussion of what's in:

Aircraft Deicers
Asphalt
Baseballs
Bug Sprays
Cement
CheeseWhiz
Chocolate
Erasers
Fluoride
Food Preservatives
JELL-O
Hair Coloring
Ink
Licorice
Lightsticks
Lipstick
Lycra/Spandex
MSG
New Car Smell
Opal
Paper
Pasteurized Foods
Pencils & Pencil Lead
Self-Tanners
Soap Bubbles
Shampoo
Shower Cleaners
Silly Putty
Sunscreens
Teeth Whiteners

Chemistry Mysteries

The Tell-Tale Bullet
Fox River Fish Kill
Saint's Blood
Eagle's Last Flight
Biosphere II
Buried in Ice
Flight 143
Lindow Man

Information on Science Fair Projects

How to pick a topic
What if the project has been done before?
What materials are needed?
How should you record what happens?
What if the results are not as expected?
What goes into the written report?
Nine tips for making a great display.
What happens at a science fair?

Careers
Agricultural Chemistry
Analytical Chemistry
Biochemistry
Biotechnology
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Hydrothermal Vents and Giant Tubeworms

Background Information

More on "extremophiles"

It is only relatively recently that scientists have discovered that life cannot only exist but can actually thrive under conditions that previously were thought to preclude any possibility of survival. For centuries it was assumed that life could only develop under what might loosely be called "normal" conditions. Some of these conditions included pH values not too far removed from a neutral pH of 7, ionic concentrations not too far removed from that of blood plasma, and temperatures that were not too extreme, especially on the hotter side.

There were some early hints that life might be more adaptable than what was assumed. Early in the 20th century, salt cod were spoiled by organisms that were able to tolerate the high salt concentrations used to preserve the fish. These organisms came to be called halophiles (salt loving microbes). In the 1940s acidophiles (acid loving) were discovered in the highly acidic drainage from certain mines. Then in the 1960s hyperthermophiles (heat loving) organisms were found living in the geysers and fumaroles of Yellowstone National Park.

For more information on the general topic of extremophiles, see the *ChemMatters* issue of Dec. 1999.

More about hydrothermal vents

Hydrothermal vents have been associated with the formation of new oceanic crust. They contain a great number of minerals. It is assumed that these minerals have been dissolved from rocks that lie deep beneath the vents. Since the solubility of most (but not all) minerals decreases with decreasing temperature, these minerals precipitate out when the hot water emerging from the vent encounters the colder ocean water. Many of these precipitating minerals are dark in color, so the resulting plume resembles black smoke emanating from the vent—thus the "black smoker" name. Common emitted materials include various sulfides and other compounds of lead, cobalt, zinc, copper, and iron.

There are other types of smokers as well, including "white smokers," that emit streams of gypsum (calcium sulfate, $CaSO_4$) and zinc compounds rather than sulfides.

Not only can hydrothermal vents at different locations have different chemistry, but a given hydrothermal vent or even an entire field of vents will often change their chemistry over a time period that can be as short as a few days or as long as thousands of years. To date scientists have not determined what causes this to happen.

Although hundreds of hydrothermal vents have been discovered and studied, about 99% of suspected vents have yet to be investigated. They have been found in just about every possible type of location where the sea floor is spreading its boundary. It doesn't seem to matter whether the spreading is occurring rapidly, slowly, or at some rate in between.

Scientists have given very picturesque names to many discovered hydrothermal vents. Included are:

Garden of Eden
East of Eden
Lucky Strike
Broken Spur

Snake Pit
Statue of Liberty
Eiffel Tower
Clam Acres
Snow Blower
Godzilla, so named because it is exceptionally large—150 ft high and 40 ft across. It is not the largest, however. One black smoker a few thousand miles east of Miami at a depth of 3,650 meters (11,972 feet or about 2.27 miles) is 160 feet high and 600 feet in diameter. Perhaps larger ones will be discovered by the time you read this.

A great trivia question might be to ask what all the above names have in common! How many people would realize that these names represent a list of hydrothermal vents?

There is a great deal of circulation that occurs to produce a hydrothermal vent. Lava eruptions that occur on the sea floor can produce deep cracks that can extend up to a mile or more into the lower crust. A series of dikes and passageways will form inside these cracks. Sea water rushes along these passageways, is transported downward, where it comes in contact with hot rocks or magma. Because of the immense pressures on the ocean floor, this water can become very superheated—as high as 350 ^{o}C. From there it rushes to the surface, makes contact with the cold ocean water, deposits its minerals, and voila—you have a hydrothermal vent.

Scientists are reaching the opinion that hydrothermal vent circulation is not just interesting, but may in fact have great importance. Some estimate that the circulation of seawater through the oceanic crust may be responsible for about 34% of the total heat input into the world's oceans and perhaps as much as 25% of the total global energy input. It is also thought to play a large role in determining the composition of seawater.

More on hydrothermal vent communities

As the article points out, hydrothermal vent communities were discovered in 1977. While this probably predates the birth of our students, it certainly is a relatively recent scientific discovery, especially when one considers that these communities have probably been in existence for a long period of time.

And tubeworms are hardly the only species that have been discovered. Incredibly, over 300 new species have been identified.

These species have one thing in common. They do not rely on photosynthesis, either directly or indirectly for survival. Unlike most earthly creatures that either engage in photosynthesis directly or else obtain their energy from things that do engage in photosynthesis, these creatures utilize bacteria called *chemoautotrophs* for their survival, as discussed in the article.

The existence of plumes of very hot water along the ocean floor has been known since at least 1972, and perhaps even earlier. A more detailed study of water samples taken along the Galapagos Rift suggested that the hot water was being produced by some kind of vents.

Enter the submersible "Alvin" (see *Anticipating Student Questions*).

Alvin's exploration of Rose Garden, the most famous of the hydrothermal vents, discovered not just tubeworms, but also giant clams, mussels, and other creatures, as mentioned in the article.

The discovery of this abundant and complex life at the bottom of the ocean caused us to rethink many of our basic assumptions about what is necessary for an ecosystem to exist. It had always been assumed that any life that existed deep in the ocean would, of necessity, have to rely on food that fell from above. The basics behind that assumption were that all life was ultimately dependent on photosynthesis, either directly or indirectly. Since no light can reach deep into the ocean, this meant that organisms living there would have to depend on debris that fell from above for food, either the remains of once-living creatures or their feces. Since the amount of this material is by its very nature somewhat limited, it was also thought that the amount of deep-sea life that could exist would be relatively small. Thus the discovery that vast amounts of divergent life existed came as a shock. Indeed, when one compares the density of organisms that surround hydrothermal vents to those regions of the ocean floor where life must depend on food falling from above, one finds that the density of life around hydrothermal vents is 10,000 to 100,000 times greater.

The article does a nice job of explaining the chemistry by which the creatures and organisms living in an around hydrothermal vents obtain the energy necessary to maintain life. The bacteria that are capable of utilizing hydrogen sulfide as an energy source are called chemoautotrophs. Their name is indicative of how they function—chem (they derive their energy from chemicals)—auto (they synthesize their own food)—troph (type of feeding). One can contrast them to photoautotrophs like plants and algae that obtain their energy from the sun. Basically these sulfur-oxidizing bacteria oxidize compounds like hydrogen sulfide. The oxidation reactions release energy, which is stored in the form of ATP (adenosine triphosphate), as it is in all living organisms. This energy is then used to transform carbon dioxide into simple sugars, similar to what happens in the plant kingdom. It is important to note that not only energy is needed, but also a source of electrons to reduce the carbon in CO_2 to organic molecules. The sulfides supply both.

The bacteria and creatures such as the tubeworm exist together in a true symbiotic relationship. The tubeworm (or other creature) provides a house in which the bacteria can live and the bacteria in turn provide the energy-rich carbon compounds needed for the survival of the tubeworm. The exact mechanism by which all this occurs is not fully known. Somehow the tubeworm manages to collect all the chemicals needed by the bacteria, including sulfur, oxygen and carbon dioxide. The bacteria then take these chemicals and transform them into sugars or some other energy-rich molecules needed to sustain the life of the tubeworm.

Other creatures that live around hydrothermal vents may utilize entirely different procedures to insure survival. Some, like the blind Atlantic vent shrimp, feed on the bacteria directly. Others, including some crabs and fishes apparently simply feed on other organisms that have died. A true food web exists. First are the primary producers, the chemoautotrophic sulfur bacteria, then the secondary producers like tubeworms, mussels, clams and shrimp, and finally the predators such as fishes and crabs.

The Rose Garden is no more

The Rose Garden described in the article no longer exists. A 2002 expedition designed to determine how the vent field had changed on the silver anniversary of its discovery found that lava flows had paved over the field. However, a new field was being established nearby. A community of small clams and mussels already was in existence along with one-inch tubeworms growing on larger tubeworms. Scientists named the new field Rosebud.

Connections to Chemistry Concepts

A look at a chemosynthetic reaction

The article presents an unbalanced representative “equation” for a chemosynthesis reaction:

$$CO_2 + H_2O + H_2S + O_2 \text{ -----> } [CH_2O] + H_2SO_4$$

If we take the first product to be glucose, $C_6H_{12}O_6$, two interesting challenges appear.

(1) Balance the equation, and (2) Estimate the enthalpy change for the reaction

The unbalanced equation would be:

$CO_2 + H_2O + H_2S + O_2$ -----> $C_6H_{12}O_6 + H_2SO_4$

Somewhat surprisingly, your Teacher's Guide Editor was able to balance this equation rather quickly by "inspection," but trying to present a well-laid out explanation of how it can be balanced by some rigorous and specific application of either algebraic equations or methods such as the use of oxidation numbers escaped solution. Calling upon the ChemEd ListServe for assistance, it turns out that this particular equation does not have one unique set of coefficients that will balance it, but rather actually has an infinite number of such sets. For example, one relatively straightforward set that works is:

$6CO_2 + 6H_2O + 6H_2S + 6O_2$ -----> $C_6H_{12}O_6 + 6H_2SO_4$

But two other sets that also work are 6,6,4,2,1,4 or 6,6,5,4,1,5

It turns out that if you try to achieve an algebraic solution by simplify setting the coefficient of $C_6H_{12}O_6$ to 1 and using a, b, c, d, and e for the remaining coefficients you end up with only four nondegenerate simultaneous equations but five unknowns, which evidently indicates that the problem does not have a unique solution. From a chemical perspective, this ambiguity arises because this "reaction" really describes two independent reactions—reduction of CO_2 and reduction of O_2—and the proportion of the two reactions taking place is arbitrary.

A few things should be noted here. While the unbalanced equation that appears in the article is intended to convey the general idea of the kinds of chemical reactions that chemoautotropic bacteria utilize, it should not be taken as THE equation for the process. For example, we know that elemental sulfur is often at least one of the products from this process, so other equations could have been presented as well.

Using the balanced equation presented above, we can estimate the value of ΔH for this reaction by calculating it from the enthalpies (heats) of formation of the reactants and products. This is really only an estimate, since the products are going to be produced in solution rather than in their pure state, and both temperature and pressure are not standard.

If we assume the following approximate values for enthalpies (heats) of formation:

ΔH_f CO_2 = -393 kJ/mol ΔH_f $C_6H_{12}O_6$ = -1275 kJ/mol

ΔH_f H_2O = -286 kJ/mol ΔH_f H_2SO_4 = -814 kJ/mol

ΔH_f H_2S = -21 kJ/mol ΔH_f O_2 = 0 kJ/mol

Then:

$\Delta H = [\Delta H_f\ C_6H_{12}O_6 + 6\ \Delta H_f\ H_2SO_4] – [6\ \Delta H_f\ CO_2 + 6\Delta H_f\ H_2O + 6\Delta H_f\ H_2S + 6\Delta H_f\ O_2]$

$\Delta H = [-1275 + 6(-814)] – [6(-393) + 6(-286) + 6(-21) + 6(0)]$

$\Delta H = -1959$ kJ

A couple of things may be worth noting. Unlike photosynthesis, which is an endothermic reaction, and thus requires energy from the sun in order to take place, the overall ΔH for this chemosynthetic reaction is exothermic. Nevertheless, the reaction produces glucose, a "high energy" molecule (relative to carbon dioxide and water) which creatures like the tubeworm can now utilize. On the other hand, one can generate at least one equation with an overall ΔH that is positive if you reduce the amount of sulfuric acid produced to the least possible—but this requires eliminating oxygen from among the reactants.

Chemoautotrophic bacteria are indeed aerobic; reduction of oxygen, in addition to reduction of CO_2, is required for the net chemical change to be favorable.

How water can reach a temperature of over 300 ^oC around a hydrothermal vent

The article states that water coming out of a hydrothermal vent can be at a temperature of over 300 ^oC and provides the qualitative explanation that the boiling point of water increases with increasing external pressure and the pressures present at the bottom of the ocean are extremely high. This can be shown quantitatively by use of what is called the Clausius-Clapeyron equation. This equation allows you to calculate the boiling point of a liquid at any temperature where the liquid is still capable of boiling.

The Clausius-Clapeyron equation is:

$\ln P_2/P_1 = \Delta H_{vap}/R\ (1/T_1 – 1/T_2)$

where T_1 is the boiling point at P_1, T_2 is the boiling point at P_2, and ΔH_{vap} is the molar enthalpy of vaporization of the liquid.

Let's ask the question: At what pressure will water have a boiling point of 300 ^oC?

To solve this problem, all temperatures must be expressed in Kelvin and ΔH_{vap} must be in J/mol. The numerical value of R is 8.314 J/K·mol

The ΔH_{vap} of water is 44,000 J/mol

If we assume that P_1 is 1.00 atm, where the boiling point of water is 373 K, then

$\ln P_2/1.00 = 44{,}000/8.314\ (1/373 – 1/573)$

$\ln P_2 = 4.952326$

$P_2 = 142$ atm.

So how deep do you have to descend into the ocean to obtain a pressure of about 142 atm.?

Let's assume that the density of sea water is 1.00 g/mL, since this is just an approximate calculation.

The pressure on the surface of the water is about 1 atm., so we have to add 141 additional atmospheres of pressure as we descend into the ocean.

1 atm. is the pressure exerted by a column of Hg 760 mm high.

Hg has a density of 13.6 g/mL, so it takes a column of water 13.6 times as tall as a column of Hg to exert the same pressure.

So to exert a pressure of 141 atm., it would take a column of water:

(141 atm)(760 mmHg)(13.6 mm H_2O/1 mm Hg)(1 cm/10 mm)(1 in./2.54 cm)(1 ft./12 in.)

or about 4780 feet deep.

Most hydrothermal vents are found at depths even greater than this, so it is easy to see why water emanating from a hydrothermal vent can be at temperatures in excess of 300 ^oC.

Possible Student Misconceptions

Since the article presents so much information about hydrothermal vents and the kinds of creatures that inhabit them, students may assume that these vents have been thoroughly explored. It is actually estimated that we have only discovered perhaps 1% of the total number of hydrothermal vents that probably exist.

Students may assume that the submersible Alvin was built so hydrothermal vents could be explored and is only used for that purpose. In fact Alvin predates the discovery of hydrothermal vents by several years and has been used for quite a diverse number of projects, including locating an H-bomb that fell into the ocean when two planes collided.

Demonstrations and Lessons

1. This might be a good time to perform a demonstration showing how the boiling point of a liquid is dependent on the external pressure. The classic one involves placing a beaker of water under a bell jar and then using a vacuum pump to evacuate the air from the jar. The water will boil when its vapor pressure becomes equal to the pressure inside the jar—approximately 24 mmHg at room temperature. The water will boil vigorously—students naturally think it has become hot, even though there is no source of heat. But when removed, it is not hot at all—it actually is cooler than its original temperature, since it is the "hotter" molecules that escape when a liquid boils.

2. Depending on the level of sophistication of both your course and your students, this article provides a nice opportunity to work some problems involving Hess's Law and/or the Clausius-Clapeyron equation. See *Connection to Chemistry Concepts* for some sample calculations.

Connections to the Chemistry Curriculum

Although the principal focus of the article lies more in the area of biology, there is a nice tie-in to several chemistry concepts. The fact that the water being emitted from a hydrothermal vent can be at a temperature as high as perhaps 350 ^{o}C connects to the boiling point of water, how it depends on external pressure and perhaps even the phase diagram for water if your course includes that topic. The precipitation of minerals when the hot water emitted is rapidly cooled when it meets the cold ocean water ties nicely to how the solubility of most ionic solids decreases with decreasing temperature. Depending on the level of sophistication of the course, this discussion could involve quantitative calculations of solubility at different temperatures given the K_{sp}s at different temperatures or the thermodynamic information required to calculate them. If your course includes a discussion of enthalpies of formation and Hess's Law this can be used to estimate the amount of energy released in a chemosynthesis reaction similar to the one presented in the article. Advanced courses might even include a discussion of the Clausius-Clapeyron equation and how it might be used to estimate the ocean depth needed to raise the boiling point of water to something like 300 ^{o}C.

Suggestions for Student Projects

1. Although the article focuses on tubeworms, there are a great number of fascinating creatures that live around hydrothermal vents. For example, there are "blind shrimp." They have no eyes, so it was assumed that they could not detect light. But Cindy Lee Van Dover, one of the scientists mentioned in the article, noticed a pair of reflective spots on the back of these shrimp. Students might find it interesting to learn more about either these "blind shrimp" (who actually are not completely blind) or some other unusual creature (unusual from our point of view—we probably would be considered unusual to them!).

2. Although not directly connected to hydrothermal vents in any way, students might find it interesting to prepare a report on the Cave of Movile. This 300 meter cave, discovered in 1986 in southern Romania near the shores of the Black Sea, represents one of the most unusual and isolated ecological regions in the world. Entirely above ground and isolated from the photosynthetic world for an estimated 5 million years, it is the home of 48 different invertebrates, 33 of which have not been found anywhere else on Earth. Like life around a hydrothermal vent, this ecosystem depends on chemoautotrophic bacteria.

Anticipating Student Questions

1. Why was the submersible discussed in the article named "Alvin?"

   The name was a contraction of the name of one of the persons who was instrumental in the creation and development of submersibles, Allyn Vine of Woods Hole Oceanographic

Institution (WHOI). The team using this particular submersible started to informally call it “Alvin,”—also the name of one of the three chipmunks (Simon, Theodore and Alvin) who had some popular musical “hits” (by virtue of a speeded up recording) around that time. Although not everyone was enamored of retaining Alvin as the final and official name for the submersible, the name stuck.

2. Was Alvin built just to look for hydrothermal vents?

   No. Alvin was commissioned on June 5, 1964. It has seen a great amount of service in many diverse missions, including locating an H-bomb that fell into the ocean when two planes collided.

3. If a tubeworm doesn’t have a mouth, how do the bacteria get inside?

   During the earliest stages in the development of a tubeworm it actually does have a mouth and gut that allow bacteria to enter. Later on, as the worm grows, its mouth and gut disappear, but by then the bacteria are already trapped inside.

4. Is it possible to actually visit the Rose Garden described in the article?

   No. Even if you were able to in some way hitch a ride on Alvin or some similar submersible, the Rose Garden no longer exists. See *Background Information*.

Web Sites for Additional Information and Ideas

A complete history of Alvin and its many exploits can be found at:

http://www.marine.whoi.edu/ships/alvin/alvin_history/alvin_history.htm

There are many excellent Websites relating to hydrothermal vents and the creatures that live there. A few good ones include:
http://www.oceansonline.com/hydrothe.htm
http://www.geotimes.org/july02/NN_vents.html
http://www.ocean.udel.edu/deepsea/level-2/geology/vents.html

The Website for the Woods Hole Oceanographic Institution is:
www.whoi.edu

The Mystery of The Pockmarked Paint Job

Background Information

More on the history of SEMs

The Scanning Electron Microscope was preceded by something called the Transmission Electron Microscope, or TEM. It basically operates in a manner very similar to an optical microscope, but instead of light, it uses a focused beam of electrons to “see through” a sample. Max Knoll and Ernst Ruska developed this microscope in Germany in 1931.

If you are interested in learning more about the operation of a TEM, go to:
http://www.unl.edu/CMRAcfem/temoptic.htm

It wasn’t until 1942, eleven years later, that the first non-commercial version of the SEM was created. The delay centered around the fact that the SEM requires that the electron beam be scanned across the sample, row-by-row, and this turned out to be difficult to accomplish. In fact, the first scanning microscope developed was actually a modified TEM, basically a scanning transmission microscope, or STEM. It was built in 1935.

The early SEMs were not considered to be great technological breakthroughs. They could only achieve resolutions of about 50 nm. This did not compare favorably with the rapidly developing TEMs, so further development was delayed. Then, in 1948, several researchers at Cambridge University in England took up the challenge of developing a better SEM. By 1952 they had created an improved version. This essentially is the instrument mentioned in the article. While the resolution remained at about 50 nm, the instrument was capable of producing the kind of dramatic three-dimensional images that we associate with modern SEMs.

A photograph of this early SEM can be found at:
http://mse.iastate.edu/microscopy/highschool.html

The first commercial version of the SEM appeared in 1965.

Two good Websites for additional information on the history of the development of the scanning electron microscope can be found at:

http://www-g.eng.cam.ac.uk/125/achievements/mcmullan/mcm.htm
and
http://www2.eng.cam.ac.uk/~bcb/history.htm

Types of SEMs and their cost

There are actually several different specific models and types of SEMs. The JEOL corporation is one of the major producers of SEMs, so they were contacted to obtain accurate information as to the different types of SEMs that can be purchased, the basic differences between them, and the relative costs.

Charles H. Nielsen, Vice President and Product Manager was generous enough to reply to our request for information. He indicated that there were four different types, with different models as indicated below:

Type 1 Conventional tungsten high vacuum SEMs:
Models 6060, 6460, 6460: difference is chamber and stage size

Type 2 Conventional tungsten low vacuum SEMs

There are the same as above, but include a feature that lowers the vacuum to eliminate charging of samples. This allows one to look at wet, unprepared samples. They include 6060LV, 6360LV and 6460 LV.

Type 3 Conventional thermal field emission SEMs
These are higher resolution SEMs using a field emission source. These often are referred to as analytical SEMs because they are very stable and generate high X-ray fluxes for chemical analysis. The two models are JSM-6500F and 7000F.

Type 4 Semi-in-lens cold cathode field emission SEMs
These are the highest resolution SEMs. The cold cathode produces the finest probe size, especially at low accelerating voltages. The semi-in-lens description refers to the position of the sample surface relative to the objective lens. This position allows the magnetic lens to pull the secondary electrons off the surface and direct them to a detector. Models are 6700F and 7400F.

So how much do these cost?

The starting price for the 6060 is $65,000. The 7400F starts at $444,000. But Nielsen points out that usually attachments are purchased like X-ray detectors and/or backscattered electron detectors that can increase the price by up to $100,000.

The most expensive SEM is used in the semiconductor industry for electron-beam lithography. It sells for $12 million.

And we sometimes have trouble ordering a few boxes of beakers!

Preparing a sample for an SEM

Before a sample can be placed in a scanning electron microscope, it must be properly prepared. As mentioned in the article, the sample must be contained in a high vacuum. Otherwise, the electrons that are designed to scan the sample would instead collide with gas molecules inside the instrument. This means that biological specimens have to be dried in a special way that prevents them from shriveling. And since they are going to be illuminated with electrons, they also have to be electrically conducting.

So how do you make something like a mosquito conducting?

You coat the sample with a very thin layer of gold using a special machine called a *sputter coater.*

Obtaining an image

Once the sample is properly prepared, it is placed inside the microscope's vacuum column. The column is sealed by an air-tight door. The air is then pumped out of the column. Then the electron gun shoots a beam of high energy electrons through a series of magnets. When a charged particle moves through a magnetic field its path is bent. Because of this, these magnets are able to bend and focus the electron beam to a very fine spot. Near the bottom of the instrument, where the sample sits, a set of scanning coils moves this highly focused beam back and forth across the specimen basically in a "row by row" pattern.

As discussed in the article, as this electron beam hits each spot on the sample, secondary electrons are removed from the surface of the sample. These electrons are counted with a detector that then sends the signals to an amplifier. These signals can then be interpreted to produce a final image based upon the number of electrons that are emitted from each spot on the sample. It's similar to viewing an object with light. When light bounces off an object, we obtain an image of the object. When secondary electrons are emitted from the surface of an object an instrument can "see" these electrons and convert this information into the kind of image we can see with our eyes.

Why SEMs are such a popular and useful instrument

SEMs are not cheap. Cost can range from several tens of thousands of dollars to several million dollars. So why are they so popular (see *Anticipating Student Questions*)?

Reasons include

- They can produce highly magnified images, up to several thousand times.
- They produce images of very high resolution, i.e., very closely spaced features can be distinguished.
- They have a very large *depth of field*. This means that it is possible to keep a large amount of the sample in focus at one time. This is similar to normal photography, where a large depth of field means, for example, that both a person and the background of a photograph can both be in focus.

Preparing samples for placement in an SEM is relatively easy.

More on the operation of the SEM

The article does a nice job of presenting the basic principles and specifics that underlie the operation of the scanning electron microscope. Of course it is possible to delve more deeply into the topic if time and interest permit.

It is easy to find Websites devoted to these kinds of explanations. One of the better ones is found at:
http://mse.iastate.edu/microscopy/choice.html

What makes this site especially useful is that it allows you to select three different levels of explanation, elementary school, high school, and college. In addition, the diagrams presented seem to be among the easiest to follow and understand.

One point that perhaps could use some clarification is that the basic image obtained from an SEM is obtained from the release of the secondary electrons and their detection. Backscattered electrons and X-ray analysis provide additional information about the atomic makeup of the sample being studied.

Connections to Chemistry Concepts

There is a very fundamental physical reason why there is a practical limit to the degree of magnification that can be achieved using a light microscope. One principle of optics is that even if you could build perfect lenses and had perfect illumination, light simply cannot distinguish objects that are smaller than about half the wavelength of the light you are using.

One way to try and get this idea across to students is to ask them to imagine trying to locate, i.e., obtain an “image” of an object placed in the ocean. If the object is very large, like a vertical pole with a diameter of several feet, the ocean waves will be affected as they pass over the pole, and the interaction of the wave with the pole will allow us to determine that indeed, there is something present in the ocean at that point. We have “seen” the object.

But imagine a long toothpick sticking out of the ocean. Because the wavelength of the ocean wave is so much larger than the toothpick, it will pass over the toothpick and basically not be affected. We cannot use ocean waves to locate a toothpick in the ocean. But if we could, in some way, create water waves with a wavelength of perhaps 0.01 cm, then they would be affected by this toothpick, and we could “see” them. That’s the idea of why light cannot be used to see “details” of an object if these details involve dimensions much smaller than the wavelength of light we are using.

White light has an average wavelength of about 0.55 micrometers (0.55×10^{-6} m). This is equivalent to 550 nm (550×10^{-9} m), so half that is about 275 nm. This means that we basically aren't going to be able to distinguish any feature that is too much smaller than about 275 nm. For example, if we tried to look at two lines that were closer to each other than 275 nm, it would appear to be only one line. This is called the resolution of our microscope. It just can't distinguish things smaller than that.

That's unfortunate. The interior structures of biological cells—the nuclei, mitochondria, etc., are all smaller than this and thus can't be seen with an optical microscope. Magnifications in excess of 10,000x are required. Since light microscopes had a practical limit of about 500x-1000x magnification and a resolution of around 0.2 micrometers, obviously a new type of microscope was needed. The SEM filled this need.

Possible Student Misconceptions

The article discusses the idea that a scanning electron microscope can utilize secondary electrons, X-rays, and backscattered electrons when analyzing a sample. It is possible that students may infer that all SEMs by their very nature must use all three detection techniques. While many do, the secondary electrons are sufficient to produce the image. Energy Dispersive X-ray Analysis (EDX) serves to help identify the composition of the atoms in the sample. It cannot detect very light atoms, but can detect atoms from boron to uranium. Backscattered electrons can provide useful topographical information, especially useful for specimens with smooth surfaces, but their most important role is to identify the element being bombarded. While the kind of information provided by X-rays and backscattered electrons might not be crucial if you were trying to obtain an image of a mosquito, it would be very valuable information if you were attempting to ascertain the composition of something like the paint contaminant discussed in the article.

Demonstrations and Lessons

While the actual operation of a scanning electron microscope and the theory that underlies its operation are certainly interesting, what probably amazes most people are the incredible images that can be obtained from this instrument. It is very easy to find striking images on the Web that could be brought into class, examined, and hopefully used to spark some excitement amongst students. A few good Websites for photographs are:

http://www.mos.org/sln/sem/sem.html
http://www.pbrc.hawaii.edu/bemf/microangela/
http://k12science.ati.stevens-tech.edu/curriculum/sem/unionhill/semimages.html
http://www.physics.unc.edu/~rsuper/research/gallery/misc.html

Connections to the Chemistry Curriculum

There are a number of nice curricular connections to this article. Any discussion of the operation of a scanning electron microscope is likely to include the operation of a light microscope and the inherent limitations the use of visible light imposes on magnification and resolution. This will quickly lead to a discussion of the nature of light—its frequency, wavelength, etc. The interaction of the beam of electrons with the sample and the subsequent emission of secondary electrons and X-rays quickly gets one to a discussion of atomic structure, energy levels, and the relationship between the energy of a photon of light and it frequency and wavelength.

Suggestions for Student Projects

1. Although the article does a good job of laying out and explaining, as much as possible, how the scanning electron microscope works and how it produces an image, much more involved and thorough explanations are possible. Advanced students or students with either a knowledge of physics or an aptitude along these areas might enjoy learning more about how the SEM operates and how it captures an image. Since trying to explain something to someone else is often the best way to see if you understand it yourself, they could attempt to explain these principles of operation to their classmates, many of whose background knowledge may not be as extensive.

2. While it isn't very likely that any students would actually be able to access and work with an SEM, such a notion is not beyond possibility (see *Anticipating Student Questions*). Several science centers around the country offer this kind of SEM exposure to high school students. Included are the Boston Museum of Science as well as Fernbank in Atlanta. If you are fortunate enough to be located near one of these centers, a project centering around the use of an SEM might make for a fascinating report.

Anticipating Student Questions

1. Is there any way that a high school student could ever actually get to see and/or use a scanning electron microscope?

   Actually there is. For example, the Museum of Science in Boston, MA has a program whereby for $20 students can enroll in a seven-hour class where they are able to learn about the SEM, learn how to prepare samples for the SEM, and actually operate the SEM. After completing the program students will actually be in possession of a photograph of a sample that they have prepared.

2. How many SEMs are in use across the world today?

   Over 50,000. Interestingly enough, early on in the development of the SEM the question arose as to whether there might actually be some commercial value associated with the instrument, i.e., would there be buyers who would want to purchase one? A team of marketing experts was hired to estimate the potential demand. After conducting a careful study, they estimated that perhaps 6-10 might potentially be sold.

   Charles H. Nielsen of the JEOL corporation (see *Background Information*), indicates that they sell approximately 1500 SEMs every year.

3. What's the highest magnification that can be achieved by an SEM?

   There is always the possibility that something better may exist by the time this is read, but the LEO 1530 SEM can achieve a magnification up to 3,000,000x.

Activity Picture

Releasing the POWER of Oxygen!

What to expect

Photo by Mike Ciesielski

Insertion of the glowing splint into the high O_2 environment of the flask causes it to burst into flame.