Sniffing Landmines

RONOCO CONSULTING CORPORATION

By Sarah Vos

Outside a U.S. military airbase in Kandahar, Afghanistan, eight teams of landmine detector dogs work through the desert brush searching for explosives. Insurgents had surrounded the airbase with landmines—buried explosives that blow up when a person steps on them or when a car drives over them.

Each dog works with its own handler. The dogs walk away from their handlers, sniffing in a straight line for 30 feet and then sniff their way back to the handlers, following the same line. Sometimes, one of the dogs sits and looks at a spot on the ground. By sitting, the dog indicates to the handler that an explosive is present.

Each time a dog finds a landmine, everyone else is pulled out of the area until "Explosive Ordnance Disposal" teams that are trained in handling hazardous devices containing explosive materials determine what the dog has found—an active or exploded landmine, a partial landmine, or another piece of explosive. Then they destroy any active explosives by setting them off.

In the spring of 2005, the dogs helped identify some 2,000 landmines over three months on the perimeter of the Kandahar airbase, saving human lives and clearing the way for an expansion of the base.

Throughout the world, dogs are increasingly being used to detect landmines to supplement the use of traditional metal detectors. Because of their strong sense of smell, dogs can detect very low amounts of vapor released by the landmines, thus helping to remove them safely.

PFC. RENATO LARA

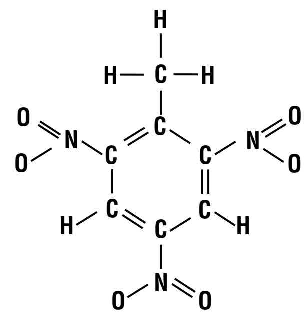
A Marine covers rear exits during a search of a residence in Rawah, Al Anbar Province, Iraq.

But not all dogs can do it and their training is uneven, prompting scientists and the federal government to develop programs to improve the training of these dogs and to find ways to select the most successful dog breeds. Other scientists have been trying to understand how dogs smell, hoping to make detectors that are as sensitive as a dog's nose in detecting explosives.

Cheap and dangerous

Landmines are cheap explosives buried close to the surface so that anyone or anything walking on them—even a dog or a child—will set them off. Landmines have been used in many war-torn countries by governments and rebel groups alike. When they explode, landmines maim and kill. Their presence cuts off access to water and prevents the use of agricultural land. They close down roads and paths and terrorize local inhabitants.

Landmines are made of a metal or a plastic casing that contains an explosive, usually the chemical trinitrotoluene (TNT).



TNT

When a landmine is set off, it causes a chemical explosion that spontaneously releases a large amount of hot gas. As the gas expands, it creates a shock wave that destroys anything it hits as it moves forward in every direction.

Near the explosion site, the shock wave from the explosion can travel as fast as 32,000 kilometers per hour (and then slows down rapidly with distance, becoming a sound wave). The shock wave causes molecules to break into fragments, which then recombine into stable gases, such as nitrogen (N_2), water (H_2O), and carbon dioxide (CO_2).

For example, when TNT ($C_7H_5N_3O_6$) is detonated, it decomposes into nitrogen (N_2), water vapor (H_2O), carbon monoxide (CO), and carbon (C):

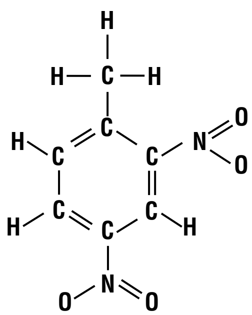
$$2\,C_7H_5N_3O_6 \rightarrow 3\,N_2 + 5\,H_2O + 7\,CO + 7\,C$$

In this case, the shock wave travels at 25,000 kilometers per hour, and the carbon forms the soot that is typical of a TNT explosion.

Escaping through the soil and into the air

When a landmine is buried underground, small amounts of the explosive inside escape through the casing either underground or into the air in the form of vapors. Dogs usually smell the vapor.

Some chemicals tend to release molecules into the air readily, making them easier to detect. This is the case with TNT, which releases an impurity called 2,4 -dinitrotoluene (DNT) that is easier to detect than TNT.



DNT

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Landmines and unexploded munitions found in Afghanistan.

In 1998, investigators at the Canine and Detection Research Institute (CDRI) at Auburn University, Auburn, AL, used this result to show that when dogs find a TNT landmine, they actually have learned to sniff DNT—not TNT—to detect landmines. This discovery later helped in the design of instruments for detecting landmines. Auburn University has one of the most extensive and comprehensive U.S. programs of research and technology development related to the use of dogs for the detection of explosives and other hazardous materials.

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A dog can smell chemicals up to a million times better than humans.

Dogs vs. metal detectors

The most common way to search for landmines is with metal detectors, a time-consuming process since metal detectors cannot distinguish between unexploded landmines, shrapnel, and other explosives. Also, during the past 30 years, more and more mines have been made of plastic, making metal detectors nearly unusable.

The second most common way to search for landmines is through specially trained dogs.

"Dogs can search an area a lot faster than a man with a metal detector," says Dan Hayter, president of Global Training Academy in Somerset, TX, a private company that, for the past 22 years, has been training dogs to detect bombs, mines, and drugs.

The teams working in Kandahar were supervised by Hayter. Dogs work best when they can narrow down the locations of suspected landmines, Hayter says. Then, when his teams find four or five landmines in close proximity to one another, Hayter calls metal detector teams to check the area.

The reason dogs are so successful at detecting explosives is that their sense of smell is more developed than that of humans.

"Compared to dogs, humans use their eyes more than their nose," says Paul Waggoner, director of CDRI. "Dogs are much better at smelling things but they don't use their eyes as much as humans do. They are odor-guided animals."

Scientists have shown that dogs can smell chemicals up to a million times better than humans. For example, while humans can usually smell hydrogen sulfide at a concentration as low as 10^{-6} %, or 0.000001%, a dog is able to smell that same chemical at a concentration as low as 10^{-13} %, or 0.0000000000001%.

Are landmine-detecting dogs reliable?

For the past 25 years, Larry Myers, a professor at the University of Auburn's College of Veterinary Medicine, has been trying to figure out what dogs smell. He has done experiments with explosives, illegal drugs, and substances arsonists use to start fires.

In one experiment, dogs were trained to identify gasoline. Gasoline is made up of more than 300 components, and Myers wanted to know which group of chemicals the dogs were sniffing to identify gasoline.

One year, the study showed that the dogs were tracking one group of chemicals. But the following year, Myers tested another group

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A handler leads his dog to a demining lane to detect trace levels of explosive vapors.

of chemicals on the same dogs. Surprisingly, the dogs were able to recognize this group of chemicals as being part of gasoline. The dogs had adapted, Myers explains.

Hayter trains his dogs in the United States using TNT and other explosives. Then, once overseas, the dogs are trained on landmines that have been removed from local mine fields before being deployed to actual mine fields. When TNT has been in the ground for years, the only chemical vapor available to the dogs may be DNT, although Hayter's dogs are trained on TNT.

"DNT doesn't smell like the original TNT, which is why we first use landmines that come from active mine fields so that the dogs can get used to the smell of these landmines," Hayter says. "This learning experience is critical because it allows dogs to learn the makeup of real mines that may have been in the ground for years."

Although dogs can recognize odors and improve over time, they need to be trained for a long period of time, typically for four to six months. "In our training, we make sure that when a dog has detected the explosive, it positions itself between the mine and its handler and then it sits staring at the place where the landmine is buried," Hayter says.

In turn, handlers are trained to keep a close look at their dogs and the areas being searched to watch for potential hazards that might harm the dogs. The handlers also learn to verbally encourage the dogs to continue the search and reward them when explosives are detected.

"The relationship between the dog and the handler is crucial to make it work," Myers says. "A handler needs to constantly encourage the dog and show it his or her full attention. Otherwise, the dog gets tired and distracted and can be used as little as only two hours a day."

Mimicking a dog's nose

Because of the time and efforts needed to train dogs, scientists are now trying to develop devices that mimic the dog's sense of smell.

A dog's olfactory system—both its nose and the part of the nervous system above it that is connected to the brain—works a lot like ours. When a dog comes into contact with an odor, it sniffs it. This concentrates the odor molecules and brings them up to the receptor cells in the dog's nose. But a dog has 20 to 40 times more receptor cells than we do.

Since the early 1980s, scientists have tried to mimic what goes on in the dog's nose and brain by developing odor-detection devices that are more sensitive than current sensors to various chemicals. Although these detectors have not reached the sensitivity of a dog's nose, they are currently used not only for the detection of landmines, but also to check environmental pollution and to make perfumes.

A major project called the Unexploded Ordnance Detection and Neutralization Program, sponsored by the Defense Advanced Research Projects Agency (DARPA)—the research agency of the U.S. Department of Defense—is seeking to develop a device called an electronic dog's nose that is more sensitive than current odor-detection devices. Through this program, DARPA has been funding various university projects.

In one of those projects, led by John S. Kauer, professor of neuroscience at Tufts University, Boston, MA, scientists developed such an electronic dog's nose. The internal surfaces of this nose were covered with chemicals that interact with very low levels of various explosives.

Then, in collaboration with Waggoner and a group of scientists led by Timothy M. Swager, professor of chemistry at the Massachusetts Institute of Technology (near Boston), Kauer's team tested the device at Auburn University. From 1998 to 2003, the researchers studied the sensitivity of various chemicals in the nose to DNT and TNT and found that an electronic nose covered with polymers was as sensitive as—and sometimes even slightly more sensitive than—a dog's nose. These experiments also allowed the scientists to make a computer simulation of how a dog's nose detects and discriminates various chemicals.

SGT. KEVIN L. MOSES SR.

U.S. soldiers and Iraqi soldiers conduct joint patrols in Ameriyah, Iraq. U.S. Army Spc. Robert Dami and his working dog Jay search a home for explosives.

Another team of scientists led by Gary S. Settles, professor of mechanical engineering at Penn State University, University Park, PA, is studying the airflow inside a dog nose to understand how the nose samples the air and detects very small amounts of chemicals. Settles and colleagues (who had been previously involved in Kauer's project as well) are trying to understand in detail how chemicals flow in the dog's nostrils and how the hair inside the nostrils detect chemicals and relay that information to the brain. Settles and colleagues are now using their results to simulate a detector that works the same way.

Better dogs

While research to develop an electronic dog nose and similar devices is ongoing, other efforts seek to improve the training of dogs because training programs throughout the world and across the United States vary in quality and efficiency.

The Geneva International Centre for Humanitarian Demining, a United Nations organization specializing in mine clearance and victim assistance, has developed procedures to improve the efficiency of dog training programs. These procedures suggest choosing certain breeds of dogs that are more successful than others at detecting landmines.

At Auburn University, Myers is developing a program to make landmine-detecting dogs more reliable. Although the program has not been funded yet, its goal is to optimize dog training by looking at the best ways to both stimulate the dogs and teach the handlers how to work efficiently with their assigned dogs.

JUPITER IMAGES

"The information collected over the past three decades about how these dogs behave is now helping us to devise more rigorous ways to train these dogs," Myers says. "If this program is funded, we should be able to provide guidelines to make dog training programs more consistent and more successful."

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Sarah Vos is a reporter for the *Lexington Herald-Leader* in Lexington, KY. Her most recent *ChemMatters* article, "Linus Pauling, American Hero," appeared in the October 2007 issue.

April 2008 Teacher's Guide

"Sniffing Landmines"

Student Questions

Sniffing Landmines

1. What explosive is used in the land mines discussed in the story?
2. What is the chemical formula of this substance?
3. What substances are mine-sniffing dogs trained to find?
4. What is the percentage of DNT in a typical solid sample of TNT?
5. What is the percentage of DNT in the vapor that sublimes from a typical sample of TNT?
6. What is the lowest concentration of hydrogen sulfide in the air that humans can typically smell?
7. What is the lowest concentration of hydrogen sulfide in the air that dogs can typically smell?
8. How many times more receptor cells does a dog have than a human?
9. How many different components are there in gasoline?
10. What is one pollutant can be detected in groundwater using electronic "noses"?

Answers to Student Questions

Sniffing Landmines

1. **What explosive is used in the land mines discussed in the story?**
   The explosive used in land mines in the story is trinitrotoluene or TNT

2. **What is the chemical formula of this substance?**
   The chemical formula for TNT is $C_7H_5N_3O_6$.

3. **What substances are mine-sniffing dogs trained to find?**
   Mine-sniffing dogs are trained to find trinitrotoluene or DNT.

4. **What is the percentage of DNT in a typical solid sample of TNT?**
   The percentage of DNT in a typical solid sample of TNT is 0.08%.

5. **What is the percentage of DNT in the vapor that sublimes from a typical sample of TNT?**
   The percentage of DNT in the sublimed vapor from a typical sample of TNT is 35%.

6. **What is the lowest concentration of hydrogen sulfide in the air that humans can typically smell?**
   The lowest concentration of H_2S *that humans can smell in the air is* 10^{-6} *%, or 0.000001%.*

7. **What is the lowest concentration of hydrogen sulfide in the air that dogs can typically smell?**
   The lowest concentration of H_2S *that dogs can smell in the air is* 10^{-13} *%, or 0.0000000000001%.*

8. **How many times more receptor cells do a dog have than a human?**
   Dogs have 20 to 40 times as many receptors as humans.

9. **How many different components are there in gasoline?**
   There are more than 300 components in gasoline.

10. **What is one pollutant can be detected in groundwater using electronic "noses"?**
    Trichloroethylene or TCE is one pollutant that can be detected in groundwater using electronic "noses".

ChemMatters Puzzle: A CHEM CROSTIC on the ENVIRONMENT

In the grid below is a quote from Carl Sagan in his book Billions and Billions. The passage (and many of the clues below) deal with environmental concerns as valid now as when Sagan wrote the book in the nineties. Your task is to reveal the quote from the clues provided.

To start, guess as many of the words defined below the grid as you can and write them over the numbered dashes. Then transfer those letters to corresponding numbered squares in the diagram. Black squares indicate word endings. Once you begin to get the sense of the quote, you will be able to work backwards to any clue words left unsolved on the first pass.

Hint: the answers to the clues are arranged alphabetically by first letter.

1E	2G	3J	4B		5C	6A	7H		8L	9K	10M	11E	12K	13D	14B	15E		16H
17I	18J	19M		20I	21H	22J	23M		24F	25K	26G		27A	28L	29B		30K	31I
32E	33A	34F	35E		36B	37I		38I	39H	40K	41B	42C	43E		44A	45L	46A	47M
48G	49E	50J		51F	52I	53H		54M	55A	56D	57F		58M	59L	60C	61A		

A) __ V __ __ __ __ __ __ His number is $6 x10^{23}$!
6 46 33 55 44 61 27

B) __ __ __ __ __ A concentrated solution of NaCl, especially from the sea.
41 4 36 29 14

C) __ __ __ Formula of QUICKLIME.
5 60 42

D) __ __ Symbol of the alkali metal with lowest e.n.
56 13

E) __ __ __ __ __ __ __ Gasoline's value for this is about .77 g/mL.
49 11 43 15 32 35 1

F) __ __ __ __ Classic western movie, " ____ NOON".
34 24 51 57

G) __ __ __ Prefix from the Greek, meaning "same as" or "equal".
48 26 2

H) __ __ __ __ __ Wetlands; important breeding grounds for many aquatic species.
16 39 7 53 21

I) __ __ __ __ __ __ A rating system for anti-knock properties of gasoline.
17 38 20 52 37 31

J) __ __ __ __ Ingredient of many solid fertilizers; first synthesized by Wohler in 1840's.
3 18 50 22

K) __ __ __ __ __ H I J K L M N O.
30 12 25 9 40

L) __ __ __ __ Ductility is ability of a metal to form a ___.
28 45 8 59

M) __ __ __ __ __ __ An ingredient of gasoline, $C_6H_4(CH_3)_2$.
47 58 10 54 23 19

Answers to A CHEM CROSTIC on the ENVIRONMENT

The quote is “Your car releases more than its own weight in carbon dioxide gas each year.”

A. Avogadro
B. Brine
C. CaO
D. Cs
E. Density
F. High
G. Iso
H. Marsh
I. Octane
J. Urea
K. Water
L. Wire
M. Xylene

The author of this puzzle, Dave Olney, has explored the substance of Sagan’s claim, Based on an equation for an alkane in gasoline burning and gasoline’s density, one can show by stoichiometry one gallon of gasoline generates about 20 pounds of CO_2 as it burns. Then, some order-of-magnitude calculations show that a typical two ton, fossil fuel-burning car does indeed generate more than two tons of the gas in a typical year of driving.

If any reader would like to see his analysis, he will be happy to E-mail it as a WORD attachment. Contact: djolney@verizon.net

NSES Correlation

National Science Education Content Standard Addressed

National Science Education Content Standard Addressed As a result of activities in grades 9-12, all students should develop understanding	**Question From the Classroom**	**The Quest for a Clean Drink**	**Sniffing Land-mines**	**Emma Perry Carr**	**The Chemistry of Arson Investigation**	**Chemicals in the Air**	**Interview: Gerhard Ertl**
Science as Inquiry Standard A: about scientific inquiry.		✔	✔	✔	✔	✔	✔
Physical Science Standard B: of the structure and properties of matter.	✔		✔	✔	✔	✔	
Physical Science Standard B: of chemical reactions.		✔		✔	✔	✔	
Physical Science Standard B: of interaction of energy & matter.					✔	✔	
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 natural resources.		✔				✔	
Science in Personal and Social Perspectives Standard F: of environmental quality.		✔				✔	

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

Anticipation guides help engage students by activating prior knowledge and stimulating student interest before reading. If class time permits, discuss their responses to each statement before reading each article. As they read, students should look for evidence supporting or refuting their initial responses.

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. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Sniffing Landmines

Me	Text	Statement
		1. Dogs detect landmines by the vapors that are emitted.
		2. The shock wave produced when a landmine explodes travels at the speed of sound.
		3. High explosives, like TNT, are less stable than low explosives.
		4. Metal detectors cannot detect landmines made of plastic.
		5. Dogs must be trained for more than a year to detect landmines.
		6. A dog has 20 to 40 times more receptor cells to smell odors than humans do.

		7. Scientists have developed odor-detection devices that are more sensitive than a dog's nose.
		8. All breeds of dogs are equally successful at detecting landmines.

Content Reading Guides

These matrices 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. Encourage students to use their own words and avoid copying entire sentences from the articles. The use of bullets helps them do this. 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

Notes for teachers about the articles:

1. There are several opportunities in the articles to lean more about structural formulas in this issue. If your students have not already learned about them, you may want to spend some time explaining the information they provide to readers.

2. The article about Emma Perry Carr is an excellent opportunity for your students to learn about isomers and the evidence used to determine their structures. If you have molecular model kits available to build models of the cis-trans isomers described in the reading, it would help the students understand that the double bonds cannot twist or rotate.

Sniffing Landmines

In the chart below, compare TNT and DNT

	TNT	DNT
Chemical formula		
Physical properties		
Detection by dogs		

In the chart below, list the advantages and disadvantages of using dogs to locate landmines.

Advantages	Disadvantages

Sniffing Landmines

Background Information

More on the senses and the sense of smell

The sense of sight detects light, while the sense of hearing detects compressional vibrations in the air around us. Touch senses physical pressure. Meanwhile, taste and smell respond to the specific chemical nature of substances, and for this reason they are collectively know as the chemical senses.

Much of our detailed understanding of how smell works was discovered by Linda B. Buck and Richard Axel, who independently carried out intensive studies into how olfaction, the process of smelling, works. The two scientists shared the Nobel Prize for Physiology or Medicine in 2004 for their discoveries.

Buck and Axel studied a type of cell found in the nose called olfactory receptor cells, and a family of proteins called receptor proteins found in those cells. By studying mouse olfactory receptor cells, they found that each such cell contained only one type of receptor protein. In mice there are over 1,000 different kinds of receptor proteins, although humans may possess only about 350.

Proteins are long chain-like molecules, made by joining together many amino acid molecules. Receptor proteins are found at the surfaces of receptor cells, and the proteins snake in and out of the cell membrane, crossing it seven times. In the process, receptor proteins are twisted and bent into different shapes, creating cavities of different shapes and sizes. Each receptor protein has a different cavity shape. Odorant molecules can dock with these cavities in the receptor proteins. The shape of the cavity of a particular receptor protein is shaped to allow only members of specific families of molecules to dock with it, in the familiar lock-and-key manner of protein-substrate chemistry. This means that each kind of receptor protein responds to only a specific family of compounds. While a human may only have 350 or so different kinds of receptor cells, many odors are made of combinations of substances. Humans can discern as many as 10,000 different odors, that is, 10,000 different combinations of substances. In addition, within a chemical family, different members may not bind to the same receptor protein, allowing additional levels of nuance in the smell that is perceived.

When a molecule docks with a receptor protein, the shape of the protein changes, triggering an electrical signal which is transmitted first to an organ called the olfactory bulb, which sits just over the bone that forms the roof of the nasal cavity in the skull. From the olfactory bulb, signals are then relayed to the brain where they are interpreted as odor.

A relatively large part of the genome of any given mammal is devoted to coding for receptor proteins. With so many different kinds of receptor proteins, as much as 3% or a mammal’s gene codes for the proteins involved in odor reception.

Inside the nose, receptor cells are attached to a tissue called the olfactory epithelium. In humans, the olfactory epithelium is rather small, and only covers a small part of the surface of the inside of the nasal cavity near the cavity's roof. In dogs, however, the olfactory epithelium covers nearly the entire surface of the interior of the nasal cavity. On top of this, a long-snouted tracking dog like a bloodhound or a basset hound may have a considerably larger nasal cavity than a human. All in all, the olfactory epithelium of a dog may have up to fifty times the surface area as that of a human. While a human may have around 3 cm^2 of olfactory epithelium, a dog might have up to 150 cm^2.

A dog's wet nose also helps it smell more acutely, as odorants are captured as they dissolve in the moisture. The shape of the interior of a dog's nasal cavity also allows odors to be trapped inside during inhalation, without being expelled during exhalation. This allows odorants to concentrate inside the dog's nose for easier detection. A dramatic result of all of these adaptations is that dogs can smell certain substances at concentration up to 100 million (1×10^8) times lower than humans can.

Beagles, bloodhounds, and basset hounds have been bred to have especially keen senses of smell, even for dogs. In addition to sniffing out land mines, dogs are also used to sniff luggage for bombs at airports, to find hidden drugs at border crossings, and even in medical diagnostics. Dogs are trained to detect odors, too faint for humans to smell, that indicate a diabetic patient might be about to go into insulin shock, a condition that results when blood sugar levels drop dangerously low, and can lead to coma and even death. When the dog smells insulin shock on the way, it can alert the patient to take preventative measures, like eating something sweet. If the insulin shock comes while the patient is asleep, a barking dog can be a lifesaver. In the future, dogs may also be used to smell cancers while still too small to be detected by conventional means. Since early detection can mean the difference between life and death, dog diagnostics could save many lives someday.

More on explosions

Hollywood often gives a misleading impression of explosions, when the hero jumps away from a car, or a building, or a boat just as it erupts into a giant ball of flame. The "explosions" you see in movies aren't particularly powerful explosions, but rather rapid combustion, usually of jugs of gasoline placed inside the car or whatever. This trick produces a nice big orange fireball that looks good on the big screen, but it doesn't necessarily produce a powerful explosion. For all its drama, that gasoline fireball really doesn't exert that much outward pressure, and the pressure wave is a big part of what makes an explosion an explosion.

An easy way to generate a pressure wave is to quickly produce lots of gaseous products from solid or liquid reactants. (Remember that the gasoline that gives us those Hollywood fireballs doesn't burn in the liquid phase, but only ignites after it evaporates.) Since gases exert pressure, sudden production of gases means sudden pressure. TNT is an excellent explosive because it can produce so many moles of gas per mole of reactant. The same can be said for nitroglycerin, which reacts in a similar manner to TNT. Likewise, azides can decompose to produce N_2; peroxides can break down to produce O_2. (While peroxides aren't commonly used as explosives, their explosive nature means they must be handled with care when used for other purposes.)

The sudden release of gases is a big part of what makes a good explosive, but there is another factor in the case of TNT, and other organic nitro compounds, like nitroglycerine. One thing is that they contain an oxidizer and a fuel in the same molecules. The oxygen atoms from the nitro groups can combine with the carbon atoms without the presence of external O_2 molecules. This process is exothermic, like O_2 combustion. This means the decomposition gives off lots of heat. The production of heat isn't necessary for a reaction to be explosive. Acetone peroxide gives off very little heat when it explodes, for example. However, since the pressure of a gas increases with increasing temperature, all that heat can only make the bang bigger.

In all this discussion we have been talking specifically about *mechanical* explosions. In chemistry, we can also speak of *kinetic* explosions. A kinetic explosion is a chemical reaction that proceeds by a runaway chain reaction, specifically a radical reaction in which each successive step results in more radical products than radical reactants. The chemical reactions used in blasting explosives are not necessarily kinetic explosions.

More on explosives history

The first explosive used by people was black powder, which was invented in China in around the 9th Century A.D. Black powder is a mixture of charcoal (carbon), sulfur, and potassium nitrate. The Chinese first used black powder to invent fireworks. Soon after, they developed military rockets propelled by black powder. The knowledge of black powder made its way westward rather quickly for the time, as the English monk and alchemist Roger Bacon wrote about it in the year 1260. Eventually, people in Europe and the Middle East used black powder to invent cannons.

Aside from fireworks, the use of black powder for peaceful purposes was slower to develop. By the 1800s, black powder was being used in engineering projects such as making cuts in rock for railroad construction. This was dangerous business, as black powder could often ignite prematurely, posing a serious risk for the workers who set and detonated the explosive charges. During the construction of the U.S. transcontinental railroad, many Chinese workers were killed in black powder accidents while blasting tunnels and cuts through California's Sierra Nevada Mountains.

Nitroglycerin proved to be a powerful and useful explosive during the same time period, but it suffered from the same problems as black powder, specifically that it was dangerous to handle. A shock could easily set it off, making it difficult to transport, especially in an age where smooth, paved roads were few and far between. Swedish chemist Alfred Nobel solved this problem by mixing nitroglycerin with diatomaceous earth, a form of silica, to form a paste that was much safer to handle. Nobel's dynamite was much more resistant to shock than straight nitroglycerin, and quickly become a popular explosive for civil engineering projects as well as for military use.

Another explosive was discovered by accident in 1846 when Swiss chemist Christian Schönbein accidentally spilled nitric acid on a piece of cotton. The resultant nitrocellulose found many uses. As one of the first moldable plastics to see widespread use, nitrocellulose was used to make shirt collars, billiard balls, and photographic film. However, being flammable and explosive, its use in photographic film often led to movie theater fires as nitrate film was ignited by the heat of projector bulbs. In the western U.S., there were accounts of billiard balls popping explosively on the break, hurting no one but sending cowboys reaching for their six guns. The explosive nature of nitrocellulose was quickly harnessed, and “gun cotton” soon replaced black powder as a propellant for firearms, from handguns to heavy artillery. The main advantage of nitrocellulose was that it burned without smoke, unlike black powder.

Trinitrotoluene was prepared by Joseph Wilbrand in 1863, but its roots go back to 1788, when Haussmann first prepared a similar compound, picric acid, or trinitrophenol. Picric acid is a powerful explosive, but unstable and dangerous to use. Trinitrotoluene is much more stable, and is in fact rather difficult to detonate. It requires a detonator explosive, such as lead (II) azide. (Interestingly, chemists are currently researching “green explosives” which do not contain lead.)

Connections to Chemistry Concepts

1. **Chemical reactions and reaction types**—All explosives work by undergoing chemical reaction. TNT for example, decomposes to nitrogen, water, carbon monoxide, and carbon. What’s more, many explosions are decomposition reactions, including the explosive reaction of TNT.
2. **States of matter**—Explosives work by rapidly producing gases when they react. In addition, dogs can smell the breakdown products of TNT because they are more volatile and can enter the gas phase.
3. **Stoichiometry**—All other things being equal, the more moles of gas an explosive produces, the more forcefully it will explode. For example, 2 moles of TNT produces a total of 15 moles of various gases (3 moles N_2, 5 moles water vapor, and 7 moles CO).
4. **Biochemistry**—Odorants couple with receptor proteins in the nose of a dog (or any other animal), following the same lock-and-key mechanism seen in many protein-substrate interactions. The same principle is at play in enzymatic catalysis.
5. **Entropy and thermodynamics**—In most explosives, a few solid or liquid molecules react to form a larger number of smaller gaseous molecules. This makes explosive reactions entropically favored on two counts. First, entropy is generally increased when large molecules break down into a greater number of molecules. Second, gases are generally at a higher state of entropy than solids. In addition, the enthalpy change of an explosive reaction is usually favorable too, evident by the heat given off in most explosions.
6. **Kinetics**—Explosions are by definition rapid reactions.
7. **Kinetic-molecular theory of gases**—It is only because gas molecules are constantly in motion that volatile substances from land mines can ever reach the nose of a dog.

Possible Student Misconceptions

1. **"Combustion and explosion are the same thing."** *It is possible for a chemical reaction to be both combustion and an explosion, but not all combustion is explosion. (Consider the movie "explosions" discussed above.) What's more, some explosions are not combustion. For example, the explosion of TNT is a simple decomposition reaction, and oxygen is not a reactant in the process.*
2. **"Dogs smell TNT."** *As the article states, dogs smell a volatile n impurity present in the TNT called dinitrotoluene (DNT), rather than the relatively non-volatile TNT itself.*
3. **"TNT explodes easily."** *TNT is a powerful explosive, but it is very stable under normal circumstances. TNT requires powerful detonating explosives in order to set it off.*
4. **"Volatile compounds explode easily."** *Volatility is a measure of how easily a substance evaporates. A substance that is volatile and flammable can be a serious fire hazard, but volatiles are not necessarily explosives. At the same time, TNT is in fact not very volatile, despite being a powerful explosive.*
5. **"Dogs can only smell gases."** *It is true that a substance must be airborne before a dog or any other land animal can smell it. However, substances can become airborne without evaporating. Aerosols, tiny liquid droplets dispersed in the air, can also be smelled. In addition, aquatic animals that can breathe under water can smell substances dissolved in water.*

Demonstrations and Lessons

1. "Experiment: Olfactory Fatigue"—This inquiry-based lab allows students to explore their own senses of smell, and how people can become insensitive to certain smells after a period of time. The website below includes background information on how the sense of smell works, as well as pdf files of the teacher guide and student procedure, linked at the top of the page. Created by Dr. Marjorie A. Murray for Neuroscience for Kids, from the University of Washington. http://faculty.washington.edu/chudler/chems.html
2. "Designer Molecules: Esterification"—This lab activity involves the synthesis of esters found in natural products whose odors students will be familiar with. As part of the activity, students will be asked to compare the odors of the esters with their own experiences of the odors of the natural products. This is done to emphasize the fact that many odors result from the combination of several compounds, and a major odor component by itself may not fully replicate the odor of the naturally-occurring mixture. The activity is part of the *Pharmaceutical Achievers* modules from the Chemical Heritage Foundation. http://www.chemheritage.org/EducationalServices/pharm/chemo/activity/ester.htm
3. Baking soda and vinegar "explosion."—Fill a film canister about 1/3 full with vinegar. Add a spatula tip full of baking soda and quickly cap

the canister. Stand back and watch while the build-up of CO_2 gas inside the canister makes the lid pop off and fly into the air. The reaction of sodium bicarbonate and acetic acid isn't normally considered "explosive". The production of CO_2 gas isn't really rapid enough, and it must be contained in a film canister to allow enough pressure for an "explosion" to build up. Even so, this simple activity demonstrates an important aspect of an explosive reaction: the production of gases. In the interest of safety, please make sure students are several feet back from the film canister.

4. Nitrogen triiodide explosive on video—While nitrogen triiodide is easily prepared from aqueous ammonia and iodine, many school districts may frown on making and detonating explosives in the classroom these days. A safer alternative is to show this demonstration on video. The demo was featured on the PBS television program *Wired Science*, Episode 101, in a segment titled "Dangerous Science." This segment is available for viewing online. http://www.pbs.org/kcet/wiredscience/video/82-dangerous_science.html
   Nitrogen triiodide exemplifies a basic principle of explosive chemistry in that it works because it easily decomposes into gaseous products. The decomposition reaction is:

   $$2\ NI_3 \rightarrow N_2 + 3\ I_2$$

Student Projects

11. Investigating explosives—Assign students or groups of students different explosives and prepare reports on them. The reports should include such information as the chemical reaction of the explosive's action, and the particular application of the explosive. The reports may be in the form of written reports, presentations, or posters.
12. Investigating fragrances—Assign students or groups of students different common fragrances (such as fruits or perfumes) and ask them to report on information such as the chemical substance or substances responsible for the fragrance, whether the active compounds can be prepared synthetically, and what some other uses for those compounds might be. The reports may be in the form of written reports, presentations, or posters.
13. What else are dogs sniffing? —Assign students or groups of students different jobs done by sniffing dogs, such as drug sniffing, bomb sniffing, search and rescue, medical diagnosis, etc. Ask the students to report on what chemical compounds are smelled by the dog in each case, what concentrations the compounds are present in, and what concentrations would be necessary for humans to smell them. The reports may be in the form of written reports, presentations, or posters.

Anticipating Student Questions

1. **“Are the dinitrotoluene fumes poisonous to the dog?”** *The U.S. Occupational Safety and Health Administration (OSHA) has established a permissible exposure limit (PEL) for DNT at 1.5 milligrams per cubic meter (mg/m^3) of air for a worker being exposed to that level for eight hour work day. In the outdoors where land mine sniffing would take place, concentrations are not likely to reach these levels just from the small amounts of DNT present in the TNT in a land mine. What's more, a dog would not likely be sniffing the same land mine for eight hours straight. On the other hand, a beagle is much smaller than a human, and safe exposure levels would be proportionately lower. Even so, the concentrations of DNT in mine fields are probably below safe exposure levels.*

1. **“Why can't you just hose down a mine to keep it from exploding?”** *Water can smother combustion by removing oxygen from the fire (but don't use it on an oil fire!), but explosives don't necessarily work by combusting. TNT does not require oxygen to explode, so water would not keep it from exploding.*
2. **“Why can't dogs smell TNT?”** *Dogs can smell TNT, but as the article says, the fumes coming off a land mine are much richer in DNT than in TNT. This is because DNT sublimes faster than TNT does, that is, DNT has a higher vapor pressure. Because TNT gives off more DNT fumes than TNT fumes, it just makes more sense to train dogs to sniff for DNT, rather than TNT.*
3. **“Are there odorless explosives?”** *Yes. Acetone peroxide, the explosive used in the July 7, 2007 London Underground and bus bombings, has little odor and has long been difficult to detect with sniffing dogs. However, because this explosive is so unstable, it is unlikely to be used in land mines.*

References

The Nobel Prize in Physiology or Medicine 2004: http://nobelprize.org/nobel_prizes/medicine/laureates/2004/index.html

Brown, G. I. *The Big Bang: The History of Explosives*. Sutton Publishing, 2000.

Fenichell, Stephen. *Plastic: The Making of a Synthetic Century*. Harper Business, 1997.

Serpell, James ed. *The Domestic Dog: Its Evolution, Behaviour, and Interactions with People*. Cambridge, UK: Cambridge University Press, 1996.

“The Dog's Sense of Smell”—from the Alabama Cooperative Extension System, a service of Alabama A&M and Auburn Universities. http://www.aces.edu/pubs/docs/U/UNP-0066/UNP-0066.pdf

Web sites for Additional Information

More sites on the sense of smell

Nobel Prize in Physiology or Medicine 2004 Illustrated Presentations—This visual tutorial explains how the sense of smell works in an easy-to-follow manner, from the Nobel Foundation.
http://nobelprize.org/nobel_prizes/medicine/laureates/2004/illpres/

Sense of Smell Institute—The official site of the educational arm of the industry group the Fragrance Foundation contains information and news on the science of smell.
http://www.senseofsmell.org/

"Can Dogs Smell Cancer?" —This news story about how dogs can help diagnose cancer by smelling characteristic tumor odors before the cancer can be detected by conventional means comes from *Science Daily.*
http://www.sciencedaily.com/releases/2006/01/060106002944.htm

More sites on land mines

International Campaign to Ban Landmines—This is the official site of the organization aiming to ban land mines by international treaty.
http://www.icbl.org/

"Land Mines: A Deadly Inheritance" —This description of how land mines have affected children living in zones of current and past conflict emanates from the United Nations Children's Education Fund (UNICEF).
http://www.unicef.org/graca/mines.htm

How Landmines Work—Technical descriptions of land mine operation come from HowStuffWorks.com.
http://www.howstuffworks.com/landmine.htm

More sites on explosives

Versatile Explosive—This site from Los Alamos National Laboratory explores explosives in all their uses, from rockets to air bags, and the chemistry that makes them go bang.
http://www.lanl.gov/quarterly/q_sum03/explosives.shtml#airbags

"Why is Nitroglycerin Explosive?" —Part of General Chemistry Online! created by Fred Senese at Frostburg State University.
http://antoine.frostburg.edu/chem/senese/101/consumer/faq/nitroglycerin.shtml

"Acetone Peroxide - Ordinary Ingredients for an Extraordinary Explosive" —This news story abut the explosives used in the July 7, 2005 London Underground bombings comes from *Chemistry World*, a publication of the Royal Society for Chemistry.
http://www.rsc.org/chemistryworld/News/2005/July/20070502.asp

"Green Explosive is a Friend of the Earth" —news story abut lead-free detonator explosives, from *The New Scientist*, March 27, 2006.
http://www.newscientist.com/article/dn8903-green-explosive-is-a-friend-of-the- earth.html

"The Halifax Explosion" — The Canadian Broadcasting Corporation provides a website telling the story of an explosion that resulted from the collision of two ships carrying military explosives in Halifax harbor in 1917.
http://www.cbc.ca/halifaxexplosion/