[Under]Arm Yourself with Chemistry!

By Mallory Pickett

I bike to work every day. My commute is mostly downhill, but on warm days, I still work up a sweat. On one steamy day, last summer, I was in a hurry to get to an important meeting, and in my rush to get ready I forgot to put on deodorant. I got to work on time, but when I arrived at the meeting I realized I had huge sweat marks under my arms, and even worse, I smelled like a gym locker room!

Why does this happen, under our arms, of all places? No matter how sweaty my forehead gets, it never smells as bad as my armpits. Why does this particular part of our body need so much deodorizing, and what makes deodorants and antiperspirants so good at hiding body odor and stopping sweat?

The rainforest of the body

Human sweat itself is actually odorless—that's why places such as your forehead or forearm might get sweaty, but not smelly. What makes the armpit special is that it is warm and moist, making it an ideal habitat for bacteria. It has even been called the "rainforest" of the body, because it contains a large and diverse bacterial ecosystem. The microbes that live under our arms are the reason sweaty underarms smell. They feed on human sweat and excrete chemical waste, including trans-3-methyl-2-hexenoic acid ($C_7H_{12}O_2$), the compound mainly responsible for the smell.

As you spray or roll deodorant under your arms, you might believe you are depending on the deodorant's strong perfume to hide the odor—but if you count on that, you could be disappointed. The perfume in deodorants is no match for your own scent. Deodorants do more than mask odor with perfumes—their active ingredients go straight to the source and kill the sweat-eating microbes. The perfume is just an added bonus for the consumer.

Deodorants: More than just a cover-up

Before deodorants and antiperspirants were invented, the only means available to keep odor at bay were bathing and perfumes. Different civilizations throughout history have made use of one or both of these methods to varying degrees.

ISTOCK; SHUTTERSTOCK

Deodorants, which were invented in the 1860s, were a significant innovation in the effort to combat body odor because, unlike perfumes, they do more than mask your body's scent with a stronger one—they kill odor-producing bacteria. Once people discovered that diseases, such as cholera, were being spread by organisms that could only be seen by a microscope, they were eager to buy anything to disinfect their drinking water, homes, and bodies.

Entrepreneurs filed patents to clean up armpits with everything from salts to antibacterials

Entrepreneurs filed patents to clean up armpits with everything from salts, such as baking soda ($NaHCO_3$), to organic antibacterials, such as formaldehyde (CH_2O). All these ingredients kill bacteria in different ways, and at the time, most scientists did not know how they worked. Finding effective antiseptics—compounds that inhibit the growth of microorganisms—was often a matter of getting lucky, or a long process of trial and error.

Baking soda, or sodium bicarbonate, was already a popular household-cleaning agent, so it is not surprising someone tried using it to clean his or her armpits. Baking soda belongs to a special class of chemical compounds, known as amphoteric compounds, that can act as both an acid and a base. Dissolved in water, the bicarbonate ion (HCO_3^-) forms a basic solution, taking a proton (H^+) from water to form hydroxide ion (OH^-):

$$NaHCO_3\,(s) \rightarrow Na^+\,(aq) + HCO_3^-\,(aq)$$

$$HCO_3^-\,(aq) + H_2O\,(l) \rightarrow H_2CO_3\,(aq) + OH^-\,(aq)$$

But it can also act as an acid, losing H^+ to form CO_3^{2-}:

$$HCO_3^-\,(aq) \rightarrow CO_3^{2-}\,(aq) + H^+\,(aq)$$

These properties are important in your body, where sodium bicarbonate helps regulate your internal pH, and in the laboratory, where it is used to neutralize both acidic and basic spills. Because baking soda is amphoteric, it is also an effective deodorant—it can neutralize smelly microbial waste products which can be both acidic and basic.

Baking soda also raises the pH of your skin's surface, making it harder for bacteria to live there (and produce smelly waste products).

Formaldehyde was popular for centuries due to its ability to kill bacteria and fungi. It was used to treat warts and embalm, or preserve, biological specimens, including human cadavers. But it is now known to be toxic and to cause cancer, so it is no longer used in deodorants.

The first commercial deodorant was invented in Philadelphia, Pa., and it hit the store shelves in 1888. The product was called Mum, and it was marketed mostly to women. The inventor's identity is unknown, but the product still exists under the brand name Ban. Historians believe the active ingredient in the original Mum was zinc oxide (ZnO), which is still used in some deodorants today. Zinc oxide itself does not kill bacteria, but, similar to baking soda, it neutralizes the fatty acid microbial waste products responsible for body odor.

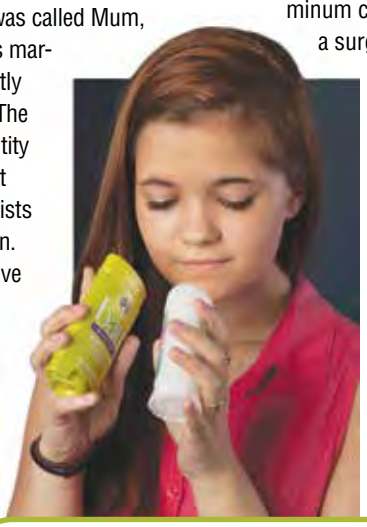
The active ingredients in modern deodorants vary widely among brands, but they are mostly divided between organic and inorganic antiseptics. The inorganic ingredients have not changed much since the 19th century—zinc oxide and baking soda are still commonly used. Many of the organic ingredients, however, are relatively new. Triclosan ($C_{12}H_7Cl_3O_2$), one common antibacterial agent, has only been in use since 1972. It kills bacteria by targeting their cell membranes and by preventing bacteria from making nutrients they need to survive.

Antiperspirants: Stop the sweat

Unlike deodorants, which kill the microbes that consume sweat and produce smell, antiperspirants fight underarm odor and wetness by blocking sweat pores. This makes armpits a dry and unappealing place for bacteria to live, and prevents embarrassing sweat marks.

Antiperspirants did not become an everyday toiletry item until around 1920, when a woman named Edna Murphey tried out an aluminum chloride ($AlCl_3$) formula her father, a surgeon, had developed to keep his hands from getting sweaty during surgery. Edna applied it to her armpits and found that it prevented wetness for up to three days! She began selling it as a new antiperspirant product, Odorono, and was the first person to successfully market an antiperspirant as an essential part of personal hygiene.

In contrast to the variety of active ingredients in deodorants, most antiperspirants con-



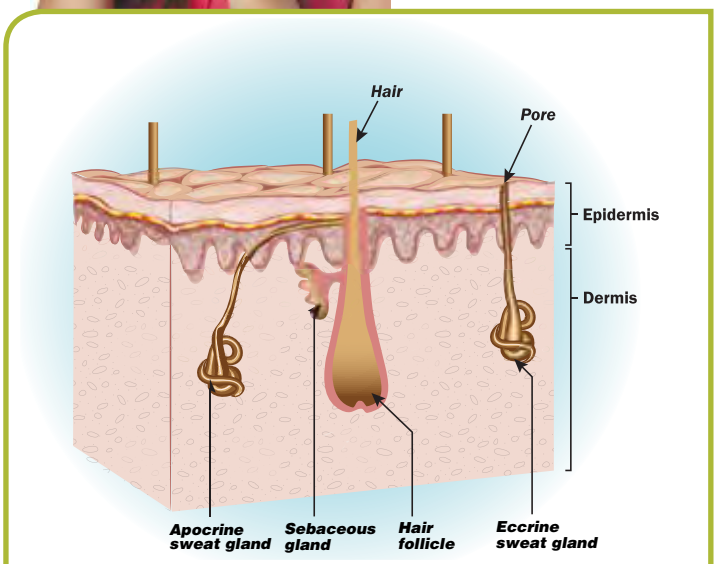


Figure 1. There are two types of sweat glands in our underarms: apocrine and eccrine glands, which are present in the two upper layers of the skin called the epidermis and dermis. Eccrine glands are more common than apocrine glands and are responsible for producing most of the sweat in our underarms and in our body.

SHUTTERSTOCK; MIKE CIESIELSKI; SHELLEY RUSSELL

tain an aluminum-based compound as their main ingredient. When these compounds are applied to your underarm, the aluminum ion (Al^{3+}) they contain works to plug your sweat ducts (Fig. 1). Scientists are not sure how this plug is formed, but the current theory is that the aluminum ions diffuse into the sweat duct and they form a gelatinous substance in the duct that blocks the sweat gland.

These plugs form in the sweat ducts because the aluminum salts in antiperspirants will stay dissolved in solution as long as the solution is acidic—like the solvent in the antiperspirant—but they will precipitate out at higher pH levels, like the more basic environment of your armpit sweat ducts. The aluminum compounds can then react with the proteins in the ducts to form the gelatinous plugs that keep your pits dry and fresh.

Different kinds of deodorants and antiperspirants

Despite their effectiveness, early antiperspirants and deodorants were a hard sell because their application was messy, and most of them would produce hydrochloric acid (HCl) in the warm environment of the armpit. Developing less acidic—and, as a result, less irritating—ingredients, along with better solvents and application methods for deodorants and antiperspirants, has been one of the main advances of modern underarm care. Solvents are the liquid, gel, or wax that the active ingredients are dissolved in, and they are important because most of the active ingredients start out as solids. To stick to your skin and be effective, they need to be suspended in some kind of liquid.

Today, the most popular solvents are silicone-based cyclomethicones, which are clear gel-like substances with low boiling points, meaning that they evaporate at low temperatures. The low boiling point is due to the nature of these molecules—they have little attraction to one another, so it takes very little heat to convert them from liquid to gas. This property is essential because it means the solvent will evaporate quickly after application to the warm armpit, and it will leave behind deodorizing or antiperspirant ingredients without any unpleasant greasiness or burning.

Perhaps the most "natural" form of deodorant, "deodorant crystals" have been used in Mexico and Thailand for hundreds of years. The crystals are usually lumps of potassium aluminum sulfate ($KAl(SO_4)_2 \cdot 12H_2O$), also called potassium alum. When rubbed on the skin, deodorant crystals work as natural antiseptics.

The general chemical form of these alum crystals is $AM(SO_4)_2 \cdot 12H_2O$, where *A* is a monovalent positive cation (an ion with a +1 charge) and *M* is a trivalent metal (a metal with a +3 charge), usually aluminum or chromium (Fig. 2).

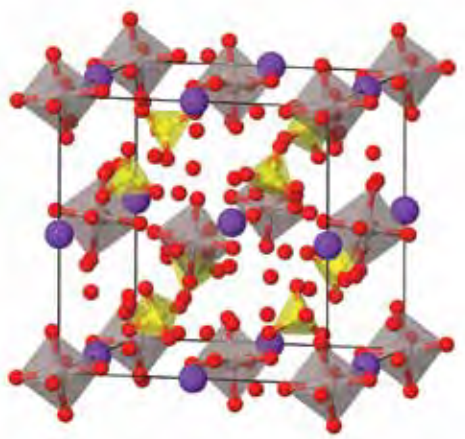


Figure 2. Crystal structure of potassium aluminum sulfate dodecahydrate ($KAl(SO_4)_2 \cdot 12H_2O$), a type of alum crystal. Oxygen atoms are represented by red spheres, sulfur atoms by yellow spheres, and potassium atoms by purple spheres. Aluminum ions are in the middle of the six-faced structure highlighted in gray.

These alums are soluble in water, and when the crystal is rubbed on damp skin, a thin layer of the alum dissolves, forming a solution of alum and water. This solution is acidic, and it lowers the pH of the armpit, creating an unfriendly environment for underarm bacteria.

Deodorants, antiperspirants, and health

I sometimes wonder, as I apply antiperspirant, if it's unhealthy to keep my body from sweating. I'm not alone in this worry—antiperspirants, ever since their invention, have been viewed with some suspicion by consumers who feel it is unnatural to block the body's release of sweat.

Scientists and consumers have raised concerns that when women shave their underarms, small cuts could allow chemicals from antiperspirants and deodorants to enter a woman's body, and that this could be related to the increasing number of breast cancer cases over the past few decades. Breast cancer researchers were worried about a group of compounds called parabens, present in both deodorants and antiperspirants. Parabens are similar in structure to the female hormone estrogen, and scientists knew that estrogen imbalances in women were related to breast cancer. Since 1999, however, numerous studies have investigated the link between deodorant and antiperspirant use and breast cancer, and no evidence has been found, to date.

In the end, whether you use deodorant, antiperspirant, or stand by your body's natural odor is your personal preference. Keeping the bacteria in your armpits, and their corresponding odor, under control, requires some maintenance—soap and water at a minimum, and using antiperspirant is the strongest option. But no matter how you approach this part of your personal hygiene, one thing is certain—there is some amazing chemistry going on underneath your arms! CM

SELECTED REFERENCES

Kimbrough, D. R. How We Smell and Why We Stink. *ChemMatters,* Dec 2001, pp 8–11.

Everts, S. How Advertisers Convinced Americans They Smelled Bad. Smithsonian.com, Aug 3, 2012: http://www.smithsonianmag.com/history-archaeology/How-Advertisers-Convinced-Americans-They-Smelled-Bad-164779646.html [accessed Feb 2014].

Handwerk, B. Armpits are "Rainforest" for Bacteria, Skin Map Shows. National Geographic News, May 28, 2009: http://news.nationalgeographic.com/news/2009/05/090528-armpits-bacteria-rainforests.html [accessed Feb 2014].

Mallory Pickett is a science writer who lives in La Jolla, Calif. This is her first article in *ChemMatters.*

PHOTO: MIKE OFSEISLSKI; FIGURE 2: AP CHEMISTRY CLASS, WESTERVILLE SOUTH HIGH SCHOOL, WESTERVILLE, OHIO, HTTP://CRYSTALS.OTTERBEIN.EDU/GALLERY/INDEX.HTML