UNIT 13: NUCLEAR CHEMISTRY

LAB	ARTICLE
#33: RADIOACTIVE DECAY OF A SWEET ELEMENT	THE NEW ALCHEMY
#34: ISOTOPES, AVERAGE ATOMIC MASS AND DECAY	VANILLA! IT'S EVERYWHERE!

The New Alchemy

By Michael McClure

In 1927, Georges Lemaitre, a Belgian priest, proposed that the universe began with a cosmic explosion of gigantic proportion. He suggested that before the explosion, there was a time when all of the matter and energy of the universe were packed together into one fantastically dense and unstable mass that he called the *cosmic egg*. A few minutes after the violent blast, protons and neutrons joined to create simple atomic nuclei. Some time later, electrons began interacting with the nuclei and atoms of the simplest elements, hydrogen and helium, were formed. As the rapidly expanding universe cooled, great clumps of gas condensed, heated up, and exploded in a burst of light. The first stars were born.

The stars were the crucibles in which nuclei were fused to form heavier elements. A star's energy comes from the fusion of nuclei as mass is converted to energy, according to Einstein's famous equation $E = mc^2$. Carbon, oxygen, neon, and all of the elements up to and including iron are synthesized during the life cycle of a star. Elements beyond iron are made when massive stars end their lives as supernovae. The nuclear reactions that produce elements beyond iron require more energy than they produce, so these elements will not form under the conditions of a normal star. But the enormous energy available in an exploding supernova is sufficient to drive nuclei and other particles together. As nuclei are forced to absorb protons and neutrons, they can grow to form elements with masses greater than that of iron, and they can continue to grow, forming elements as heavy as uranium.

The early years: Who were the players?

Billions of years later after that initial, tremendous blast, scientists in the 19th and 20th centuries would organize all of the known elements into neat rows and columns based on properties and atomic composition—the Periodic Table. In those early years, discoveries came fast and furious. It was predicted that new discoveries might one day reveal elements with masses and atomic numbers beyond uranium. What were these discoveries? Who were the men and women that unlocked the secrets of atoms and created the first transuranium (i.e., "beyond uranium") elements? Who succeeded in doing what early alchemists failed at—transforming one element into another?

Before we dive into these discoveries, let's first take a look at the basics of radioactivity.

Radioactivity

Radioactivity refers to spontaneous nuclear reactions that occur in various forms. Atoms that decay by alpha emission, for example, eject a particle consisting of 2 protons and 2 neutrons, in other words, a helium 2+ ion. The decay product, or daughter, is an element with two fewer atomic number units. For example, the isotope uranium-238 decays into thorium-234 by alpha emission.

$$^{238}_{92}U \rightarrow \, ^{234}_{90}Th + \, ^{4}_{2}He$$

Other modes of radioactive decay include beta decay, positron emission, and electron capture.

Radioactivity can be used as a tool for exploring the atomic nucleus. In 1919, the New Zealand-born physicist Ernest Rutherford observed the reaction between alpha particles and gaseous nitrogen atoms in a cloud chamber. The cloud chamber is a flask filled with supersaturated vapor, in this case, nitrogen gas. Alpha particles streaking through the vapor knocked electrons from nitrogen molecules, creating electrically charged ions. Vapor molecules condensed around the ions, allowing Rutherford to see the alpha particle path as a trail of tiny droplets, like the contrails of a jet aircraft.

Rutherford recorded the short tracks of many alpha particles in his experiment. Occasionally, he observed condensation tracks that were longer than expected. Because longer tracks implied less massive particles, Rutherford suggested that perhaps alpha particles were knocking out protons from the nucleus of nitrogen atoms. Gaining two protons, then losing one proton would change the nitrogen nucleus into oxygen-17. Rutherford had just observed the first artificial transmutation of an element.

$${}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}H$$

Transmutation is the transformation of one element into another through one or a series of nuclear reactions

An artificial isotope

Later on in 1934, Irene Curie-Joliot, the daughter of Marie and Pierre Curie, and her husband Fredrick Joliot performed an experiment similar to Rutherfords'. Instead of nitrogen, they used aluminum as the target. In addition to protons flying away from the collision event, they observed the emission of neutrons and some new form of radiation (called a positron emission). Surprisingly, when they stopped the experiment, neutron emission stopped, but the radiation continued. How could this be? Curie-Joliot and her husband discovered that the reaction created the artificial element phosphorus-30. This isotope does not occur in nature, and it decayed into silicon by this newly discovered form of radiation—positron emission. They had witnessed the first artificial transmutation of a stable element into a radioactive isotope, by emission of an artificial form of radiation. In 1935, the Curie-Joliot's shared a Nobel Prize for this work.

$${}^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P + {}^{1}_{0}n$$

$${}^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^{0}_{+1}e$$

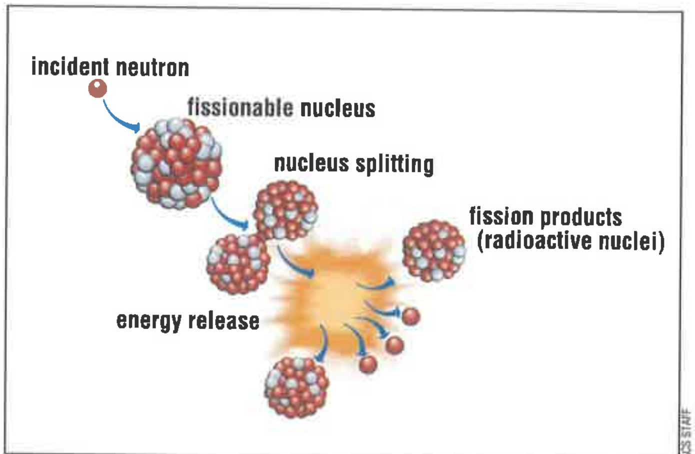
Transmutation is the transformation of one element into another through one or a series of nuclear reactions

Building new atoms and a stunning discovery

Early alchemists worked furiously trying to change one element into another, and they all came to the same conclusion: it's not easy. What they did not know is that positively charged protons inside the nucleus of every atom repel similarly charged particles. The characters of our story found that only positively charged particles with sufficient energy can overcome the strong repulsive forces and penetrate the nucleus. For this reason, Enrico Fermi, an Italian physicist, suggested that neutrons might make better nuclear missiles. Neutrons carry no electrical charge; they are neutral. Fermi and others believed that if a nucleus captured a neutron, it would try to correct for its neutron excess by beta decay, turning a neutron into a proton, thus creating an atom with an atomic number increased by one unit. Suppose uranium, the heaviest known naturally occurring element, could be forced to capture a neutron. This might make the uranium nucleus unstable and radioactive. If the unstable nucleus decayed by beta emission, a new element beyond uranium would be created.

Fermi and his collaborators bombarded uranium-238 (atomic number 92) atoms with slow neutrons. Other research groups were performing similar experiments. Initially, everyone claimed success in creating a new element with atomic number 93. But the mass of the product did not agree with the expected mass of element 93. Furthermore, its chemical properties seemed surprisingly like barium, an element much lighter than uranium. Lise Meitner, an Austrian physicist, was troubled by these findings. Looking closely at the results and making detailed calculations she came to the astonishing conclusion that uranium nuclei were splitting into smaller fragments! In seeking new elements beyond uranium, Fermi and others had stumbled upon the process of atomic fission. This discovery and the subsequent development of nuclear weapons and nuclear reactors impacted all of humanity.

Today, we know that Fermi's uranium sample contained trace amounts of uranium-235, a rare isotope that undergoes atomic fission when bombarded with neutrons. What Fermi and others did not realize was that element 93 had actually formed in the experiment, but was undetectable in the complex mixture.



The process of nuclear fission.

A planetary element

The emission of alpha particles creates a recoil effect. This causes the product isotopes to fly away from each other and deposit some distance from where the decay event occurred. American physicist Edwin McMillan in the Radiation Laboratory at the University of California, Berkeley, wanted to know exactly how far the fission products would travel through matter. His experiment was simple. First, he stacked thin sheets of paper together to form a small book. On the top sheet he placed a sample of uranium salt. Next, he exposed the salt to a source of neutrons, which induced fission. As expected, the fission fragments traveled through the paper sheets stopping at various layers in the book. McMillan could determine the location of each fission product by separating the pages and measuring the radioactivity with a Geiger counter. But in addition to finding various fission products scattered among the pages, McMillan detected two separate beta activities in the topmost sheet. Two isotopes were not recoiling with the other fission fragments.

McMillan reasoned that perhaps not all isotopes of uranium undergo fission. Maybe uranium-238 was indeed capturing a neutron, as Fermi had suspected, and decaying into a new element. In 1940, Philip Abelson, another American physicist from the Carnegie Institution in Washington, went to Berkeley to help McMillan identify the mysterious beta activities. Soon they had successfully separated and identified the first transuranium element. They named the element neptunium (Np).

$$^{238}_{92}\mathrm{U} + ^{1}_{0}n \rightarrow ^{239}_{92}\mathrm{U}$$

$$^{239}_{92}\mathrm{U} \rightarrow ^{239}_{93}\mathrm{Np} + ^{0}_{+1}\mathrm{e}$$

Why name #93 neptunium? First take a guess, and then look to the end of the article for the answer.

The search went on...

McMillan suggested that the second short-lived beta decay product in the mixture might be an element with atomic number 94. The American scientists Glenn Seaborg, Arthur Wahl, and Joseph Kennedy were working on the World War II Manhattan Project with McMillan and decided to test his idea. First, they had to overcome two difficult problems. In McMillan's experiment, only small amounts of uranium-239 and neptunium were formed. And the long half-life of the unknown isotope made it difficult to measure its activity. Seaborg's group knew they would need to synthesize larger quantities of neptunium if they were to be successful in identifying the mysterious product. They solved these problems with the help of (American physicist) Ernest Lawrence's proton merry-go-round—the cyclotron. Lawrence's cyclotron could accelerate particles to enormous speeds, imparting enough energy to overcome the repulsive forces inside an atomic nucleus. Using the cyclotron, they produced large quantities of neptunium and then watched as the neptunium decayed into an element with atomic number 94. Seaborg's group was able to show that element 94 was radioactive, emitting alpha particles with a half-life of 90 years. After the tradition of naming elements for the planets, element 94 was named plutonium.

C&EN

Glenn Seaborg

McMillan moved on to other projects, but between 1944 and 1974, Seaborg's group discovered nine additional transuranium elements. A few were synthesized in ever larger and more powerful cyclotrons, and some in nuclear reactors. Two new elements, einsteinium and fermium, were discovered in the nuclear fallout during thermonuclear weapons testing in the 1950s.

GETTY IMAGES

Revamping the periodic table

Where did the transuranium elements fit into the Periodic Table? Scientists soon learned that many transuranium elements had properties similar to the transition metals. In 1944, Seaborg proposed his Actinide hypothesis. He predicted that thorium, protactinium, uranium, and the first 11 transuranium elements would form a series of chemically similar elements following actinium (atomic number 89), similar to how the lanthanides follow lanthanum. Much research into the chemical properties of the transuranium elements has confirmed Seaborg's hypothesis.

CERN

Seven-kilometer–long accelerator in French and Swiss country side near Geneva.

The search continues ...

Today, 111 elements are listed in the Periodic Table. There are 19 transuranium elements named after planets, countries of discovery, and scientists. And elements beyond atomic number 111 have been reported but remain unconfirmed and unnamed. Will there be an end to the discovery of transuranium elements? Will scientists reach the hypothesized "Island of Stability" where theory predicts elements with atomic numbers as high as 126 may be stable? No one knows the answers. But we do know the search will continue, and perhaps you might be involved. Larger accelerators will be built to smash atoms. New detectors will allow researchers to track and interpret the zoo of particles that form when atoms collide. And each new discovery will increase our understanding of the world around us, including you and me!

Mike McClure worked for several years as a chemist at a veterinary diagnostic laboratory, investigating unusual animal deaths. He now teaches chemistry at Hopkinsville Community College in Kentucky and is a regular contributor to *ChemMatters* magazine.

Vanilla! It's Everywhere!

From steamy Mayan jungles to cold Norwegian pulp mills ... from the Aztec halls of Montezuma through Europe to Thomas Jefferson's plantation, one spice has been there. Chocoholics step aside, it is vanilla that reigns supreme as the world's most widely used flavoring!

By Gail Kay Haines

It's almost unbelievable the number of things vanilla is in. Vanilla can be produced from peanuts, grapefruit, cloves, rice bran, and even barrels of crude oil. Originally discovered in Mexican orchids, it has spread from a taste hoarded by royalty into the flavor in everybody's ice cream sundae. Vanilla is the world's most widely used flavoring, a long-believed aphrodisiac, and a contributor to the manufacture of specialty drugs.

A trip through the average home turns up vanilla in vanilla extract, room spray, soap, body lotion and massage oil, pudding mix, vanilla-scented candles, potpourri, and, of course, vanilla ice cream—the number-one seller. A flood of recent television ads—like the one featuring the bouncing Pepsi truck—signal that Coca-Cola and Pepsi are going head-to-head in the battle for *vanilla* cola supremacy.

Almost every chocolate recipe calls for it. Tobacco and cattle food are flavored with vanilla, and it is even used in baby food. Where does all this vanilla come from? The United States alone consumes more than 1000 tons of vanilla beans per year, just for "high-end" products. The world demand for vanilla far exceeds the natural supply.

Growth and harvesting

In order to meet demand, planters once carried cuttings of the tree-climbing vines from Mexico to Madagascar and other tropical areas, but the vines did not set pods. *Vanilla planifolia* (old name V. fragrans), which produces 99% of the pure vanilla sold, had been pollinated occasionally by hummingbirds, but mainly by a strain of Mexican Melipona bees. No bees meant no seedbeds and no vanilla. To make matters even more complicated, each flower opens for one day only. In 1841, growers began to hand-pollinate the orchids with a sharp bamboo stick—as they still do—and *V. planifolia* flourished. In Tahiti, vines mutated into a new species, *V. tahitensis*, the other commercial 1%.

Today, each ripening vanilla pod is so valuable that it is guarded and sometimes tattooed with its own I.D. number. Picked while green, the large pods have no characteristic smell. First, they must 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, which promotes enzymatic action to develop the flavor, requires 3–8 months,

finally yielding long, skinny blackish-brown pods—each weighing about 5 grams—filled with tiny black seeds. From planting to market can take five years, making natural-grown vanilla the second most expensive flavor, after saffron.

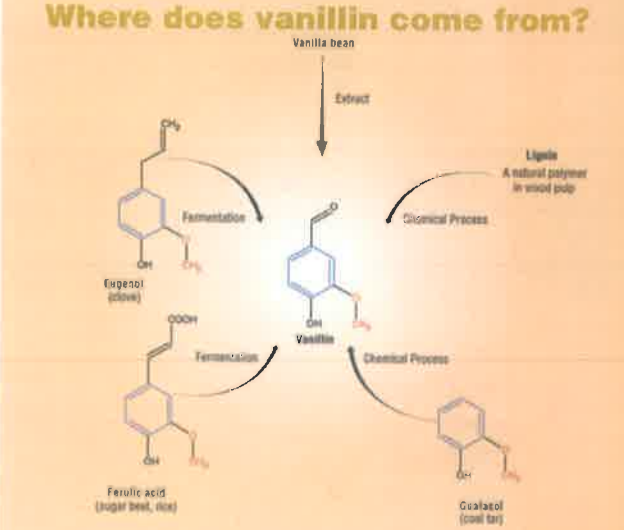
Vanillin

Vanillin, $C_8H_8O_3$, is the major component (about 2%) of "pure vanilla", a complex mixture of four primary and nearly 300 minor chemicals. All four major compounds belong to the group called "aromatics", which means they contain a benzene ring—C_6H_6—with various side chains substituted for hydrogen.

To protect consumers, different types of vanilla have specific legal meanings. *Vanillin* is only slightly soluble in water, but it dissolves easily in ethanol (ethyl alcohol). Pure *vanilla extract* is made from chopped vanilla beans, soaked for days or weeks in dilute alcohol. It is the only flavoring to have a U.S. Food and Drug Administration 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". The extract picks up hundreds of chemicals from the vanilla pod, giving "pure" vanilla its complex taste.

But vanillin is vanillin, whatever the source. In the 1880s, German chemists synthesized it as a cheap substitute for vanilla. "Imitation vanilla" is mainly synthetic vanillin. "Natural" vanilla is vanillin from other food sources mixed with a little pure extract. Since the price differences are huge, chemical tests exist to make sure each product is what the label says. But words do not always mean what they suggest. For instance, "vanilla bean" ice cream may contain, not tiny seeds, but flecks of ground pods left over from the extraction process. Vanillin

Where does vanillin come from?



Legal Vanillin and Counterfeit Extract

Because synthetic vanillin is so much cheaper than natural vanillin and not subject to the fluctuations of supply and price that affect natural foods, it offers an inexpensive way for a food producer to impart a vanilla flavor to a food or beverage. Substituting synthetic vanillin for natural vanilla is safe, sensible, and legal—as long as the product is properly labeled as containing artificial vanilla flavoring.

But passing off synthetic vanillin for vanilla extract can be lucrative. A quick trip to the supermarket reveals that vanilla extract can sell for close to $3.50 per oz., whereas imitation vanilla sells for about $0.20 per oz. This presents a tempting situation for counterfeiters.

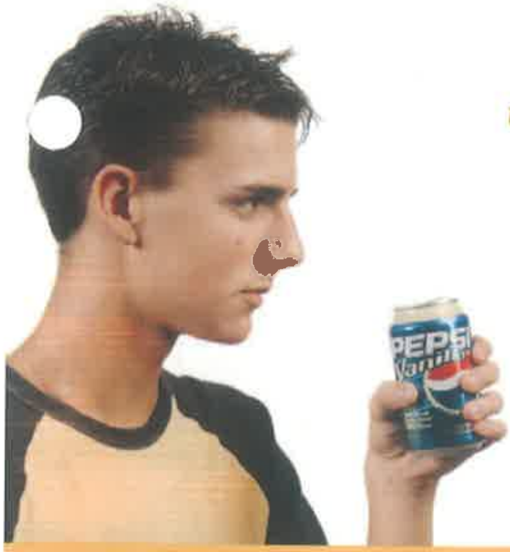
The possibility of cheating means that food chemists must devise a method to determine when a product contains natural or synthetic vanillin. But vanillin is the same chemical compound, whether it originates in the bean or is synthesized from lignin. Standard chemical analysis indicates the identity and quantity of a compound, but usually gives no clues about its sources. In the past few years, researchers have been able to distinguish between vanillin from fossil precursors, such as coal and petroleum, and vanillin of bean origin by using isotopic ratio mass spectroscopy and nuclear magnetic resonance.

The source can be determined by inspecting the carbon atoms in the vanillin with a technique called stable isotope ratio analysis (SIRA). SIRA is based on the fact that not all carbon atoms have the same mass. Of the carbon atoms found in nature, 98.9% have a mass number of 12, and 1.1% have a mass number of 13. Most organic compounds contain these percentages of carbon-12 (^{12}C) and carbon-13 (^{13}C) atoms. However, the ratio of these isotopes is slightly different for natural vanillin than for synthetic vanillin. The synthetic vanillin is enriched in ^{13}C. This happens because of differences in biochemistry of the vanilla orchid and that of most other plants.

The vanilla orchid carries on photosynthesis by a series of reactions known as the Crassulacean pathway. Most plants, however, including trees, use the Calvin pathway, which involves a greater number of chemical reactions. Because ^{13}C is heavier than ^{12}C, ^{13}C reacts more slowly—and less ^{13}C is incorporated during each photosynthesis reaction step. Most plants that will eventually become oil, coal, and lignin use the longer pathway. So synthetic vanillin from these sources has a lower percentage of ^{13}C. By measuring the ^{13}C:^{12}C ratio with a mass spectrometer, scientists at the Bureau of Alcohol, Tobacco, and Firearms have been able to identify counterfeit vanilla extract, and federal attorneys have prosecuted unscrupulous suppliers.

But the detective story does not end here. When counterfeiters discovered that chemists could tell the difference between natural and synthetic vanillin by means of isotope ratios, they searched for ways to adjust the ^{13}C:^{12}C ratio in the synthetic product to more closely match that of natural vanillin. The easiest way is to remove the $-OCH_3$ group containing ^{12}C and replace it with another $-OCH_3$ group containing ^{13}C. But the government chemists were able to spot this ploy by removing the $-OCH_3$ group and testing for the presence of ^{13}C using mass spectrometry.

Adapted from a classic *ChemMatters* article by R. C. Breedlove, August 1988



A flood of recent television ads—like the one featuring the bouncing Pepsi truck—signal that Coca-Cola and Pepsi are going head-to-head in the battle for vanilla cola supremacy.

MIKE CIESIELSKI

History

The Totonacs, in Mexico, first gathered seed pods of the wild orchid for their unique flavor. They traded pods as vine-grown "money" with the Maya, who paid the beans in taxes to the Aztecs. When Cortez invaded the New World, around 1520, his men named the pods "vainilla" (little sheath) and shipped them home as part of the Aztec treasure. From Spain, vanilla spread across Europe, sometimes as a flavoring for chocolate. Some 250 years later, when Thomas Jefferson was ambassador to France, he brought vanilla back to America. The popularity of ice cream took vanilla flavoring to the top, but chemistry brought it into everyone's life.

probably makes up the difference. And although high-fat ice creams require a higher concentration of vanillin—because there is less air to deliver the fragrance—no-fat ice creams require the most. A mixture of extract and concentrated vanillin seems to work best.

The scent in your hand lotion is likely synthetic, as is 95% of the world's vanilla supply. Once, most synthetic vanillin came from lignin—the natural polymer removed from wood pulp in papermaking. It was a good use for waste lignin, but the process gave off so much waste sulfuric acid that all such plants in North America have closed due to pollution.

Now, vanillin is more likely to be made from petroleum or coal tar. Ethyl vanillin from crude oil—which replaces the methyl (CH_3-) side chain in vanillin with ethyl, (C_2H_5-)—has a vanilla taste that is 3 times stronger than vanillin, but it is insoluble in butter, caramel, and chocolate. It is used in perfumes and low-fat ice cream. Eugenol from clove oil and guaiacol from coal tar can both be turned into vanillin. As wines and liquors age in oak barrels, alcohol pulls vanillin right out of the wood. Both peanuts and their hulls contain vanillin, which, even at parts per million (ppm) levels, adds a major flavor note. Grapefruit contains vanillin in the ppm range too, but here it causes an "off" taste. In this case, less vanillin tastes better.

MIKE CIESIELSKI

Medicinal use

Vanilla even has some medicinal uses. Vanillin is used in the manufacture of medications for Parkinson's disease and high blood pressure. Memorial Sloan-Kettering Cancer Center discovered that the vanilla-like scent of heliotropin—a compound in Tahitian vanilla—produced a 63% reduction in patient anxiety during MRI scans. Vanilla is one of the three most widely used flavoring/scents to mask the bad taste of medicine, and herbalists are reviving its popularity as a folk remedy to heal and soothe.

For hundreds of years, many people have ascribed aphrodisiac properties to vanilla. European physicians once believed that vanilla could cure sexual ailments and improve performance. Chocolate, also thought to have similar properties was considered "cold", while vanilla was "hot".

Before visiting his harem, the Aztec ruler Montezuma would consume large quantities of "chocolatl" containing vanilla extract. We'll never know if Montezuma's success with the ladies was a result of the smell of chocolate on his breath or vanilla's aphrodisiac qualities.

Maybe it's not quite that "hot", but modern research has shown men respond to vanilla more than to any other scent. Today, it is appreciated for its mood-lifting, romantic appeal to both sexes. Unless you happen to be a bug. Vanilla scent, alone or with DEET makes a good insect repellent, yet vanilla is used in flypaper, to attract flying pests. Go figure.

Either way, fans of vanilla owe a huge debt of gratitude to chemistry, for making so many sources of vanilla available. Otherwise, this "nectar of the gods", as the Totonacs called it, might still be property of the royal rich.

Gail Kay Haines is a science writer and book author from Olympia, WA.