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October 2019

Demystifying Everyday Chemistry

THE SECRET LIFE OF

GOLD

THE STORY STARTS WITH A BANG

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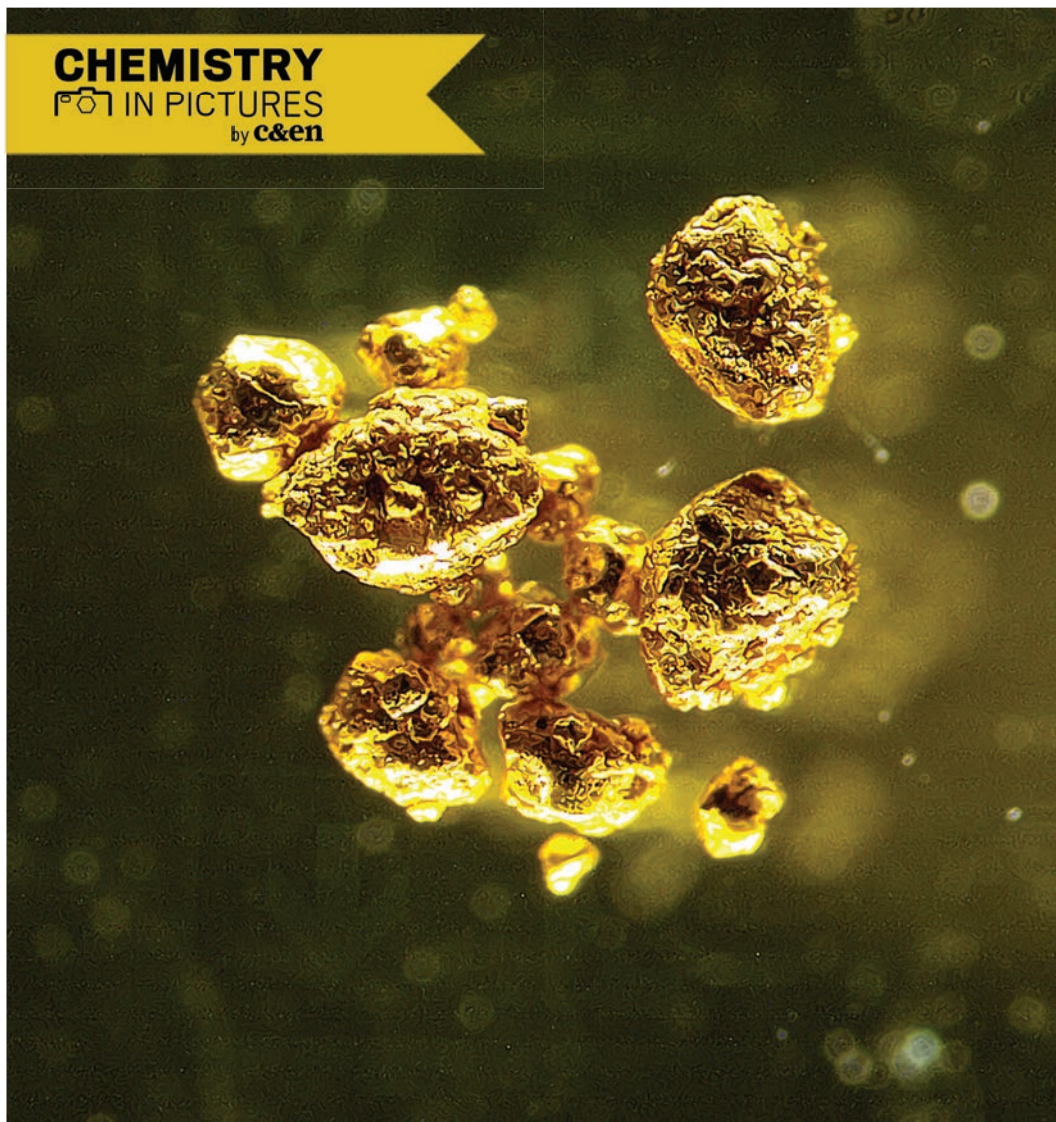
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PANNING FOR GOLD, an image from *Chemical & Engineering News' Chemistry in Pictures*

These lustrous, nearly pure, micrometer-sized gold nuggets didn't come from an underground mine like most gold you've seen. They came from solutions of processed sewage, electronic waste, and fresh water and ocean water. Researchers Wendy L. Queen, Daniel T. Sun, and coworkers at the Swiss Federal Institute of Technology, Lausanne (EPFL), have developed a way to "mine" gold from these sources to help meet global demand for the precious metal. The scientists used a composite material that pulls gold ions (Au^{3+}) from solution and reduces them to metallic gold (Au^0). The composite is then removed with heat and acid, leaving tiny, 23.9-karat gold nuggets, seen here through an optical microscope. 

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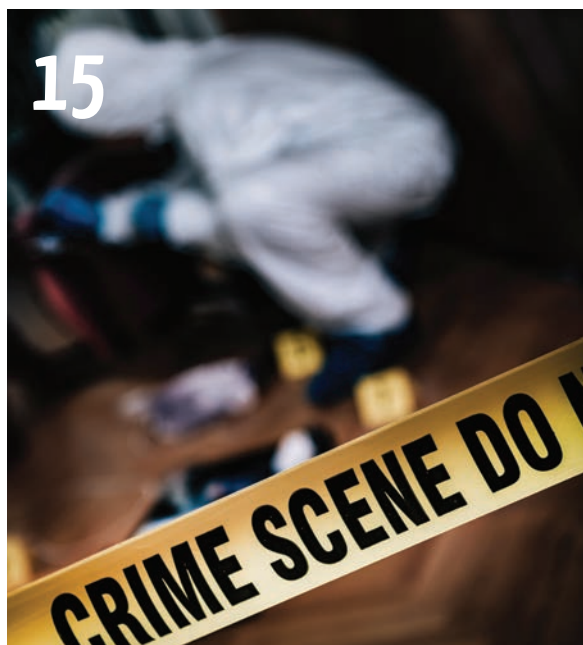
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The Asteroid Next Door

We live in a world of finite metals. What happens if we run out?

By Michael Tinneland

When it comes to commercial metals that make our cellphones and other devices function, the world is facing impending shortages that worry governments and businesses around the world. Demand for these strategic metals, such as gold, lithium, or rare-earth metals (those that are too dispersed to be mined in an economically feasible way), strains supplies. Political instability in countries where the metals are mined, in addition to trade tensions, further complicate the issue.

If we run out, there's no rushing next door—say, to the moon—to borrow more. Or is there?

The idea isn't as far-fetched as it might sound. The asteroid belt and the moon are brimming with metals. Dozens of spacecraft have already landed on the moon and Mars. Apollo missions brought back 382 kilograms (kg) of rock from the moon. In 2005, a spacecraft from Japan landed on an asteroid, collected samples, and brought them to Earth.

Big costs—bigger payoff?

To be clear, space mining would require overcoming major technological obstacles. But the

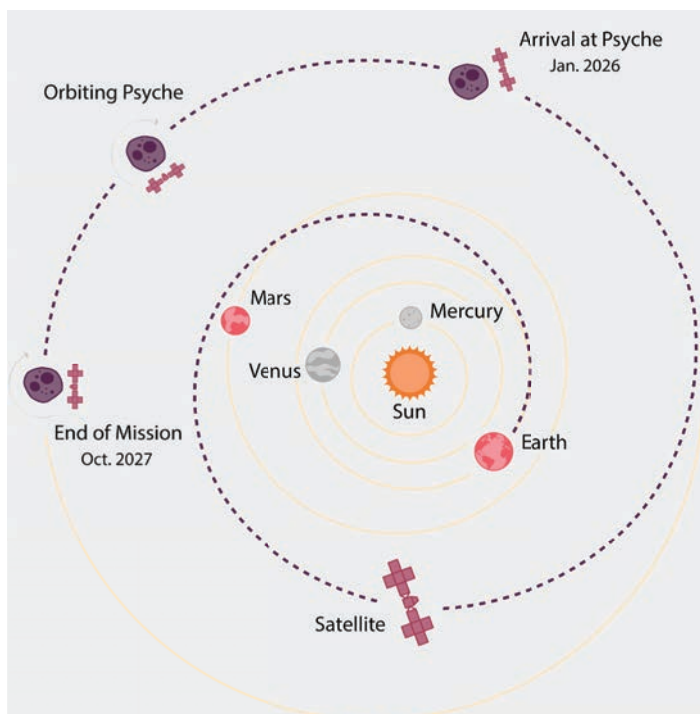
challenges haven't deterred ambitious entrepreneurs from forming dozens of private companies to set up mining operations in space.

While such ventures would be extremely costly and high risk (some have already gone under), the pay-off could be worth it. According to NASA estimates, the industry could generate revenues of \$700 quintillion. That's about 100 million times more than the total annual revenue of global mining in 2017, which was \$600 billion.

But only the most valuable materials would likely be ferried to Earth. For example, rhodium, gold, and platinum, which sell for \$70,000/kg, \$45,000/kg, and \$27,000/kg, respectively, could be among the metals worth transporting to Earth.

The rest of the material mined in space would likely remain there. Bringing back certain resources to Earth would be prohibitively expensive. Instead, the mining operations would largely be used to produce material for extraterrestrial exploration and for building colonies, such as those envisioned by Amazon CEO Jeff Bezos.

"The reason we've got to go to space, in my view, is to save the Earth," Bezos told reporters at a press conference in May announcing plans for his space company,



MAXARIASUP/RUBIN/NASA/JPL-CALTECH

⤴ This asteroid called 16 Psyche is set to receive an earthly visitor. NASA approved a mission to send a spacecraft to the metallic rock in 2022 to study its composition. Scientists know Psyche is mostly made of iron and nickel, but they speculate it might also contain other metals such as gold.

Blue Origin, to build a moon lander.

Solving side effects

Mining in space could provide solutions for the continued production of advanced technologies well into the future, and for fulfilling dreams of traveling to and living in space. But one could argue that bringing back large quantities of valuable resources might be disruptive to current markets. Gold and other precious metals are of high value because of their scarcity. If they become abundant, prices could plummet.

Oil, a

once-limited resource, became abundant with exploration. Fossil fuels have enabled development and increased living standards, while also producing pollution and contributing to global climate change. Would cheap gold cause unintended side effects?

Additionally, where some entrepreneurs, scientists, and governments see asteroid mining as a solution to our earthly resource limitations, others are calling for caution: The accessible resources in the solar system would also one day run out. And then what?

What are our other options? That is still open for discussion.

THE SECRET LIFE OF GOLD

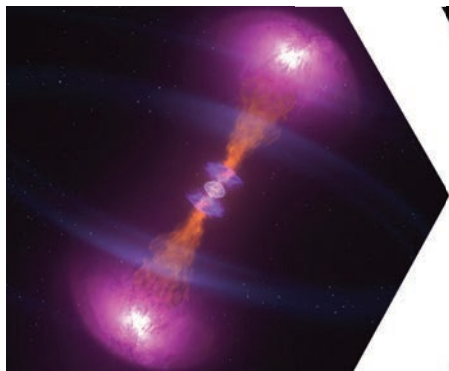
By Grant Currin

Right this second, a bit of gold could be within your reach even if you're not wearing gold jewelry. The precious metal could be in your pocket, or in front of you on your desk—that's because a very small amount of gold is inside phones, tablets, and laptops.

Hidden behind electronic screens and outer casings of glass and aluminum are computers' electronic brains, which rely on gold along with other precious metals. Just a tiny quantity of gold—about 0.034 grams—conducts electricity in a cellphone, and prevents other electrical components from corroding. It allows you to reliably text and watch YouTube videos at the tap of a finger.

That's why gold is in your pocket, but where did it come from?

FROM THE COSMOS TO YOUR COMPUTER



^ This illustration depicts the explosive merger of two neutron stars. Scientists have reported that a collision of two such stars about 4.6 billion years ago likely led to the formation of gold.



^ The flakes, fragments, and nuggets of gold embedded in Earth's crust were delivered on meteorites that pelted the planet (long before humans came along).



^ Gold is soft, highly conductive, and doesn't corrode, making it suitable for use in electronics. The electronics industry used nearly 270 tons of gold in 2018.

Star Power

For tens of millions of years, two stars involved in the creation of gold thrived on nuclear fusion. Gravity forced hydrogen nuclei in their cores to fuse, setting off additional reactions that resulted in the production of helium nuclei (or alpha particles), energy, and positrons.

The story of how gold ended up in rock formations, and in your electronics and jewelry has been murky. But researchers have been piecing together its origin story, and within the past two years, have published new reports that help flesh out where gold—one of the most valuable metals on Earth—came from.

The story starts with a bang

You may already know that the matter making up everything you have ever touched, smelled, or seen came from the Big Bang, which unzipped the universe 13.8 billion years ago. The Big Bang theory is the prevailing model of how the universe was created. It suggests that everything—all matter and energy—was jammed into a tiny point that became the universe in a massive explosion that marked the beginning of time and the creation of space itself.

At first, gold was not even a shimmery speck in the universe's explosive debut. After the Big Bang, enormous quantities of protons, neutrons, and electrons combined to form hydrogen, helium, and a little bit of lithium, says Imre Bartos, an astrophysicist at the University of Florida. These reactions seeded the universe with this cosmic dust for hundreds of thousands of years.

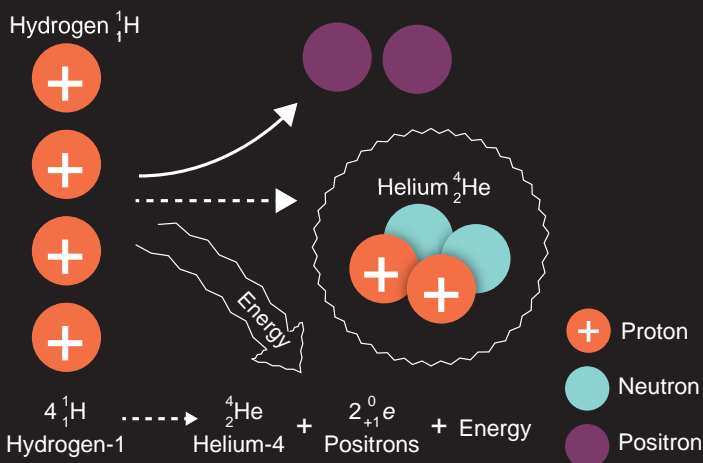
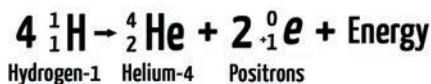
For the most part, these elements were evenly distributed across the universe. But every now and then, the density in one place was a little bit higher than the density everywhere else. When this happened, gravity began pulling atoms closer together into swirling clumps of gas and dust. As a clump compressed, its center would become dense and hot enough to start fusing hydrogen nuclei—that is, protons—together, releasing energy, and giving rise to a new star.

According to scientists' best estimates, stars began forming 13.6 billion years ago, 200 million years after the Big Bang. Gold was still nowhere to be seen.

But several billion years after the first stars were born, an important pair of large stars, each about 10 times the mass of the sun, formed and started circling each other, creating a binary star system. Bartos and a collaborator, Szabolcs Márka at Columbia University, identified the stars in 2019, publishing their work in the scientific journal *Nature*. These unnamed stars might have played a crucial role in the formation of Earth—and the precious resources, including gold, deep within our planet.

Tension

For most of these two stars' lives, they thrived on **nuclear fusion**. The stars' gravity forced hydrogen nuclei in their cores to fuse, setting off additional reactions that resulted in the production of helium nuclei (also known as alpha particles), energy, and **positrons**—the antimatter version of electrons:



RACHEL PRIGER

Nuclear fusion reactions went on for tens of millions of years. As the stars grew older, they began producing heavier elements, such as carbon, oxygen, and silicon, in their cores.

Then the stars arrived at element 26. The introduction of iron dramatically changed the course of the stars' development.

"Iron is the most stable form of matter," says Bartos. "Anything heavier than iron takes energy to create."

Ironically, it was iron's stability that spelled doom for the stars. Because the force of gravity in the core of stars is so strong, stars rely on a constant supply of energy to resist its crushing force. But with the introduction of iron, the cores stopped producing energy, inviting collapse.

Explosion

At different times, the stars' cores imploded, collapsing thousands of miles in just seconds from about the size of the Earth to about 7 miles in diameter. The implosions occurred so quickly that they created powerful shockwaves.

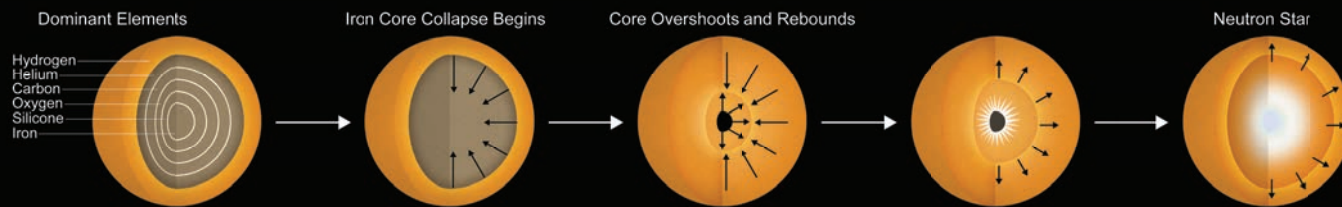
And when the cores of the stars collapsed, the outer layers also zoomed inward, crashing with the outward-bound shockwaves. The collision blasted matter out into deep space in two supernova explosions that occurred within a few million years of each other.

Remarkably, the huge amount of energy emanating from the explosions did not destroy the binary system.

"Usually, one star [in a binary system] is flung away in a supernova explosion," says James Lattimer, an astrophysicist at the State University of New York at Stony Brook.

In this case, the explosions left behind two neutron stars. Neutron stars are so dense that a single teaspoon of its material on Earth would weigh 1 billion tons.

"They're called neutron stars because after the dust has settled, they're about 95% neutrons, and 5% protons," says Lattimer, who in the 1970s was one of the first scientists to argue that neutron stars might create



A Neutron Star is Born

As a massive star ages, the formation in its core of increasingly heavy elements, such as carbon, oxygen, silicon, and then iron, leads to the core's collapse under intense gravitational force. The core's implosion blasts out a shockwave while gravity yanks the star's outer layers inward. The incoming layers crash with the outbound wave, blasting matter into deep space. The small, incredibly dense core left behind is a neutron star.



Why We Are Made of 'Star Stuff'

<http://bit.ly/Reactions-StarStuff>

heavy elements, such as gold. Decades later, new research would support this hypothesis.

Collision

The neutron stars circled each other for billions of years, inching closer to each other at a glacial rate.

And then, about 4.6 billion years ago, the long-time neighbors collided.

The crash sent clouds of neutrons whizzing into space. The particles in this cloud of debris smashed into one another, finally creating elements heavier than iron.

Among the new elements created was—at last—element 79: gold! The mass of the gold created in the neutron star collision was between 3 and 13 times that of the Earth, according to a 2018 paper in the *Astrophysical Journal*.

But the gold produced didn't appear in large chunks. Its atoms shot into every corner of the universe. Some joined an ancient cloud of dust near our corner of the Milky Way. About 100 million years later, the cloud began to condense and break into fragments. One of the fragments would become our solar system.

The vast majority of the atoms in this pre-solar nebula were hydrogen and helium, and almost all of them comprised the sun. The heavier elements joined to form asteroids and rocky planets including Earth.

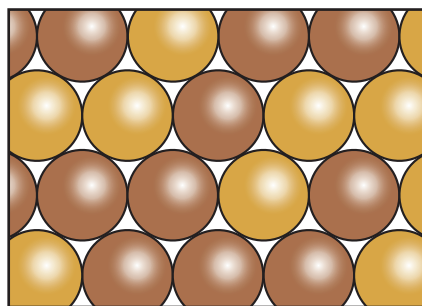
The early Earth was a ball of molten rock that created gravity strong enough to drag the heaviest elements, including gold, into its core. Scientists at the University of Bristol in the United Kingdom have calculated that the gold in the core could cover the surface of the Earth with a layer 13 inches thick.

But that's not where the gold in your phones comes from. Humans have never laid eyes on the gold in the Earth's core, and probably never will. That gold is locked away under a few thousand miles of rock.

What Does "24-Karat Gold" Mean?

Almost all gold in circulation today is an alloy—a mixture of two or more metals.

We use alloys because they are often cheaper and more useful. Gold is an expensive element, so mixing gold with less expensive metals yields less expensive alloys, which can be used to make products that are more affordable. It's also expensive to refine gold to very high levels of purity. Even the most highly refined samples contain an atom of something else for every 100,000 atoms of Au.



« White gold, rose gold, and other types of gold are mixtures of gold atoms with atoms of other metals, such as copper, nickel, and aluminum.

Alloys are also more practical than pure gold for most applications. Pure gold is very soft, so jewelers mix it with elements, such as nickel, copper, or silver, to create a stronger alloy with other desirable properties. For example, certain alloys have distinctive colors that make jewelry more interesting. White gold is often made by mixing nine parts gold to one part nickel. Rose gold is a family of alloys that contain about three parts gold to one part copper.

Karats (sometimes misspelled "carats," a measure of mass often used for gemstones) are the unit used to express the percentage of pure gold in an alloy. The number of karats represents the fraction of pure gold per 24 parts. So 24-karat gold is pure gold, while 14-karat gold is an alloy that only contains 58.3% gold (14 g of gold per 24 g of total alloy).

Currently, the mine recognized as the deepest in the world is approximately 2.5 miles below the Earth's surface.

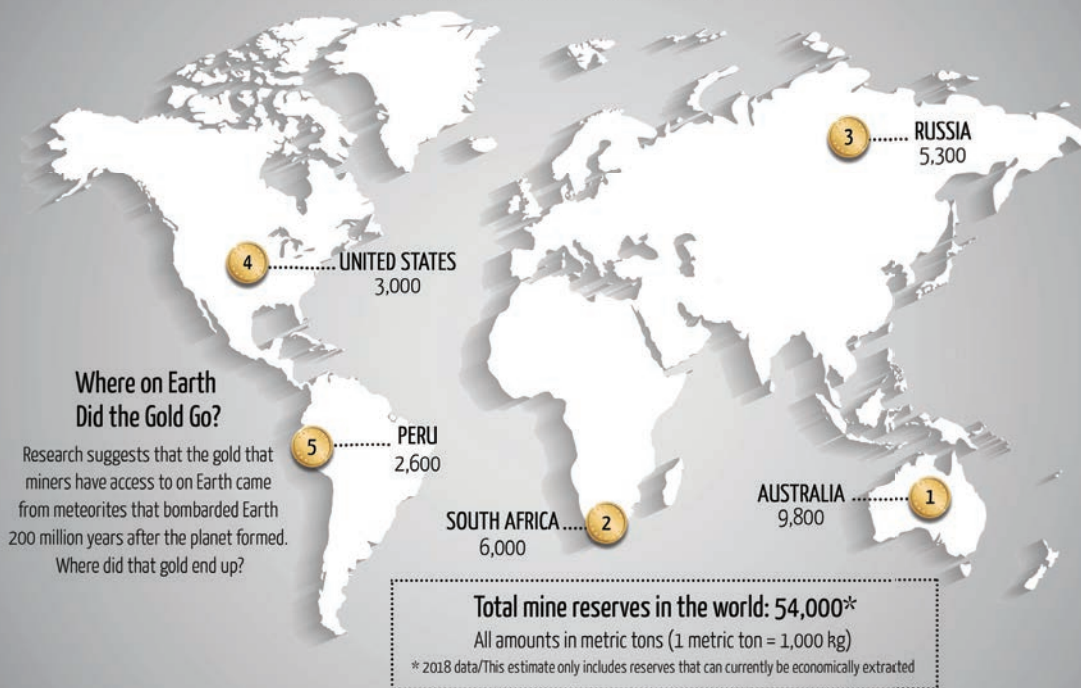
The gold that ultimately ended up in our phones, jewelry, and the world's bank reserves took a slightly longer journey to get here.

Bombardment

Much smaller than planets, asteroids and meteoroids did not lock their gold beneath tons of rock. Some of it probably sat on the surface, fused to chunks of rock.

So, about 200 million years after Earth was formed, when the planet swept through a patch of rocks floating in space, meteorites (space rocks that hit a planet's surface) pelted Earth with billions of tons of rock,

Recoverable Reserves of Gold: Top 5 Countries



KELSEY CASSELBURY

according to the researchers at Bristol. Recent research suggests that the meteorites embedded a new batch of heavy elements, including gold, in the planet's crust. The force of the collisions caused portions of the crust to melt and shift around, leaving gold in veins, which are crystalized mineral deposits within rocks, where miners find it today.

The universe in your pocket

Gold has made life more opulent for centuries with gilded statues, golden domes, and luxurious threads for embroidery. In the digital age, the lustrous metal has taken on new importance. But given gold's long history, it's clear that your phone is merely a rest stop for gold atoms that debuted in the universe billions of years ago.

Grant Currin is a science writer from Cleveland, Tenn.

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Where's the Gold?

Not only is gold beautiful, but it can also be super practical. It can be beaten into sheets 0.18 micrometers thick, drawn into wires 5 micrometers in diameter, and is inert to most acids and oxidants. Plus, it's a good conductor of heat and electricity, and forms stable, uniform nanoparticles.

Below are some of the uses of gold, but in order to read them, you have to decode the cipher. Each letter has been randomly substituted with another letter of the alphabet. The letter substitutions are the same for each word. Can you identify all the uses of gold?
(Starting hint: N stands for C, and R stands for L)

YHZHRAM _____

NEKUX _____

NDUNHA VAHDVPHUVX _____

PHBDRX _____

XPDAVLCEUH NKANFKVX _____

HRHNVAKNDR NEUVDNVX _____

DAVSKNKDR RHQX _____

AHSRHNKJH NEDVKUQ KU XLDNH CHRPHVX _____

* Answers are in the Teacher's Guide, available at www.acs.org/chemmatters.org

CASH, CHEMISTRY, AND COUNTERFEIT

By Brian Rohrig

If you earn cash from babysitting, mowing lawns, or other jobs, you might have noticed that not all bills' designs and colors are the same. That's because money has changed a lot over the years; today U.S. currency is more complex and colorful than ever before. These changes have primarily come about for one reason—to beat counterfeiting.

From currency's inception, people have tried to trick others into accepting fake money. The Aztecs, a 14th- to 16th-century culture that thrived in what is now central Mexico, used cacao beans for currency, and even these were counterfeited. People would fill empty cacao pods with clay and try to pass them off for the real thing. The oldest surviving paper banknote, dating back to 14th-century China, displays a warning that (translated into English) reads “the counterfeiter shall summarily be decapitated”—leaving little doubt about how counterfeiting was viewed in that era.

Today, producing fake money remains a serious crime. But thanks to ingenuity on the part of scientists, designers, and printers who work on banknotes, genuine cash now features several attributes to ensure that producing counterfeits doesn't pay off.

Fighting forgeries

To stay ahead of counterfeiters, governments have relied on the

brightest minds to fight the illegal practice. In early 18th-century England, Isaac Newton spent 30 years putting his considerable intellect to work in devising ways to foil counterfeiters.

Benjamin Franklin, the father of paper money in the United States (thus his visage on the \$100 bill), devised numerous ways to thwart counterfeiters. He designed intricate patterns on his bills that were difficult to copy. On one banknote, he deliberately misspelled the word “Pennsylvania,” assuming that any counterfeiter worth his salt would spell it correctly, falling for the ruse.

Despite these efforts, fake currency at certain points in history was rampant. The invention of photography in the 1830s invigorated counterfeiters' efforts. By the time the Civil War began, it was estimated that up to half of the paper money in circulation in the United States was counterfeit. In 1865, the U.S. Department of the Treasury created the Secret Service to crack down on the practice.



GETTY IMAGES



So, during the Civil War, the special green color now associated with U.S. currency made its debut: It couldn't be replicated using the black-and-white film of the day. This innovation gave rise to the term "greenbacks" for U.S. banknotes.

Simple solutions

These days, governments rely on a range of low- to high-tech tactics to fight counterfeiting.

One well-known line of defense entails testing a paper bill's material with a counterfeit-detector pen. Ordinary paper contains starch, while currency paper is made of starch-free ingredients cotton and linen. The ink in counterfeit detector pens contains triiodide ions (I_3^-) that react with starch to produce a dark purple-black color.

So, if you mark a bill printed on regular paper with one of these pens, a black mark would reveal the bill as counterfeit. However, these pens' usefulness is limited. The absence of a black mark simply indicates the absence of starch—it does not confirm a bill's authenticity.

Another simple method to test whether a bill might be real entails feeling its texture. Real bills feel rough due to the raised ink and the texture of their cotton-linen composition.

One trick that counterfeiters have used to ensure their fakes have the right texture

involves removing the ink from a \$1 bill, making it blank, and then printing the design of a \$20 bill on the note. In response, government chemists have put a lot of time and energy into formulating inks that are difficult to remove. But, interestingly, the inks never dry—if you rub a dollar bill firmly on a piece of white paper, you can see this feature for yourself! Usually, ink used in counterfeit money is water-soluble and won't rub off.

Embedding colorful fibers and impressing watermarks in paper money are other relatively easy and long-standing methods for deterring would-be counterfeiters. As early as 1928, the Crane Company, the sole supplier of U.S. currency paper, began inserting tiny, hard-to-replicate red and blue silk fibers throughout the paper. Watermarking involves impressing designs into paper. The designs are less dense than the rest of the paper, and transmit more light. Despite being a centuries-old technique, watermarking is still tough to fake.

Modern money

When deterring counterfeiters, however, it's best to keep innovating. As soon as official currency-printers come up with new forgery-suppressing tactics, counterfeiters adapt. Luckily, new technologies help governments stay ahead of the game.



Cotton Currency

Perhaps the biggest innovation in our currency involves the substrate upon which it is printed.

Today's "paper" money is not really made of paper. It is printed on a cotton-linen fabric, which can hold up better than normal paper. According to the U.S. Bureau of Engraving and Printing, which produces our currency, a dollar bill can be folded 4,000 times before it tears. The current content specification for U.S. bills is 75% cotton and 25% linen.

Other countries use different formulations; Euro banknotes, for example, are made of 100% cotton, giving them a softer feel.

Ground State
 Excited State

<https://teachchemistry.org/exciting-electrons>
 To see how UV-sensitive features in currency work, try out this online simulation created by the American Association of Chemistry Teachers. It demonstrates what happens as an electron is excited and then returns to its ground state. Drag and drop the bars next to the electron, and click the "Excite!" button (not pictured).

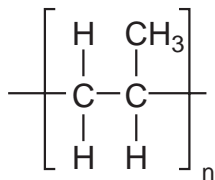
One recent innovation is the addition of **ultraviolet (UV)** features. On every U.S. banknote, beginning with the \$5 bill, thin polyester threads are woven through the bill. Under a black light, these threads **fluoresce**, and each denomination fluoresces a different color. The strip on a \$5 bill is blue, while it turns pink on a \$100 bill. Nearly every country has a variety of UV features on their money. If you have access to some foreign currency, place it under a black light to reveal vivid designs.

These UV-sensitive features are the result of special fluorescent pigments in the ink. Fluorescence is the property of absorbing one type of electromagnetic radiation and emitting another. When a black light shines on a fluorescent pigment, UV light is absorbed, which excites an electron to a higher energy level. When the electron then returns to the ground state, it emits a photon with a lower energy and longer wavelength than the photon that was absorbed. The wavelength of the released photon typically lies within the visible light portion of the electromagnetic spectrum.

Another relatively new method to deter counterfeiters involves color-changing features.



Polypropylene



Polypropylene is a polymer made of repeating units of propylene (C_3H_6).

You can find an example of this on the \$20 bill. Look for the copper-colored “20” in the lower right-hand corner of \$20s that have been printed since 2003. Tilting the angle at which you view the number will change its color to green. The effect is not an optical illusion; the ink is actually changing colors!

The technical term for this color-shifting ink is optically variable ink, which changes colors based on the angle at which light strikes it. It is made by suspending tiny multilayered particles throughout the ink. Each thin layer within these particles reflects light in different ways. The reflected light that reaches our eyes is a combination of different **wavelengths** that interfere with one another both **constructively** and **destructively**. When the angle at which light strikes these particles changes, the wavelengths of reflected light also changes. Photocopying this ink yields a single color and cannot replicate the effects of color-changing ink.

Paper or plastic

In the never-ending race to stay ahead of counterfeiters, some countries have resorted to transitioning their paper currency to plastic. These thin bills, usually made with **polypropylene** (C_3H_6)_n, look like paper but feel slick and smooth. Plastic allows for all sorts of nifty security features, such as detailed holograms and see-through windows.

In 1988, Australia became the first country to introduce plastic currency, and since then several other countries, including Britain, Russia, Mexico, and Canada, have followed suit. Since their transition to plastic banknotes, Canadian authorities have reported that the incidence of counterfeiting dropped by nearly 75%.

Despite such benefits, much of the world still uses natural materials for their banknotes.

But with the rise of digital currency such as



↗ Polyester threads woven into U.S. currency fluoresce under a black light.

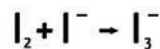


Inside the Iodine-Starch Test

Starch is a carbohydrate, consisting of two types of polysaccharides: amylose and amylopectin.

The color change observed when an iodine solution reacts with starch is caused by a **charge-transfer complex** between triiodide ions (I_3^-) and amylose. Charge-transfer complexes form when an electronic charge is transferred between two or more molecules, or parts of molecules.

Triiodide ions form in an aqueous solution according to this equation:



In the iodine-starch test, triiodide acts as a **charge acceptor**, and amylose acts as a **charge donor**.

Electrons in such charge-transfer complexes are easily excited by light to higher energy levels. Light is absorbed in the process, and its complementary color, in this case dark purple, is observed by the human eye.



PHOTO: GETTY IMAGES; GRAPHICS: RACHEL PRICER

Bitcoin and other types of online payment services such as Apple Pay and Venmo, could printed money finally be in danger of becoming obsolete? Cold, hard cash has faced threats before from credit cards, checks, and direct deposit, yet physical money has held strong. One significant reason for this reliance on physical money is that about 6.5% of households in the United States do not have bank accounts, leaving them largely reliant on cash, according to a 2017 national survey conducted by the U.S. Federal Deposit Insurance Corporation.

Given that advances have made our paper

currency more counterfeit-proof than ever before, the smart money says it will be around for many years to come.

Brian Rohrig is a chemistry teacher from Columbus, Ohio.

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The Measure of a MOLE

By XiaoZhi Lim

Counting and measuring are such essential life skills that it would be impossible to remember when we first encountered the concept of a number or measurement. Even as a baby, you started to perceive whether few or many people were near you. As birthdays passed, you learned to count money in dollars and cents, and that popularity on Instagram is measured in the number of “likes.”

In chemistry, you measure atoms, ions, and molecules in moles. The last unit to join the modern metric system known as the International System of Units, the mole is a unit that helps chemists count. Just as the word “pair” means two and a “dozen” means 12, a mole of any given thing means there is roughly 6.02×10^{23} of it.

It's such an important part of chemistry that chemists in the United States recognize 6:02 a.m. to 6:02 p.m. on October 23 as Mole Day. This year's Mole Day holds particular significance for chemists: The definition of a mole has officially changed!

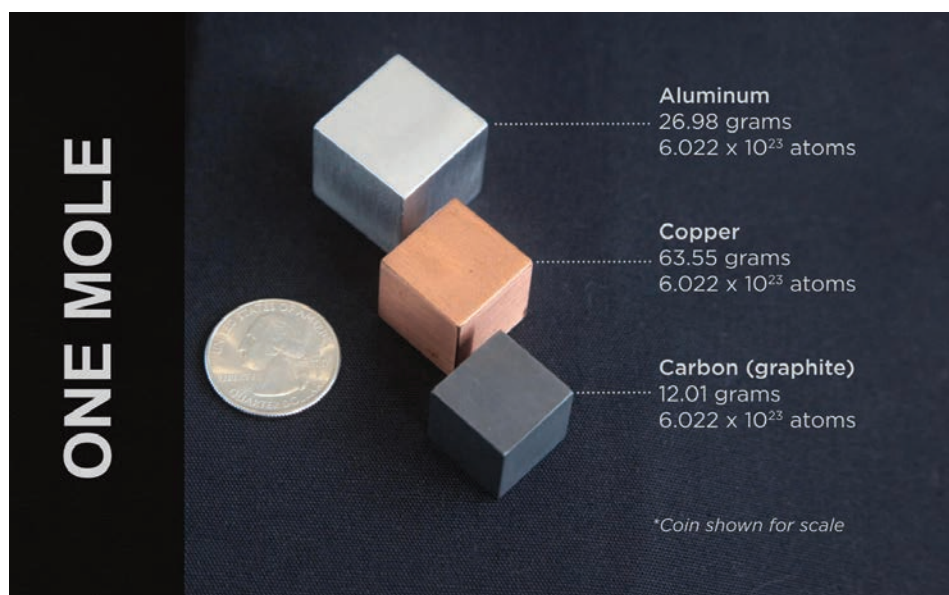
Wait, units can change?

Units of measurement seem as unquestionable as the sun's rise every morning, but even as they were established, scientists knew the units weren't perfect. Take the kilogram for example. How does a scale know how much a kilogram, or 2.2 pounds, is? Well, the kilogram was defined as the mass of a physical object: an iridium-platinum cylinder that was made in 1889. The cylinder, known as the International Prototype of the Kilogram (IPK), along with six official copies, reside under lock and key in a secure vault near Paris, France.

Despite being well protected, when the IPK was weighed for the third time in its life in 1989, it was lighter than its official copies by some 50 micrograms—about the mass of an eyelash. But technically, the IPK didn't get lighter. Its copies grew heavier because the IPK is the definition of a kilogram.

The mole had its weaknesses as well. It was defined as the number of atoms in exactly 12 grams (0.012 kilograms) of carbon-12 (^{12}C), the most common isotope of carbon. And this number depended on the definition of the kilogram.

“This connection is not wanted anymore,” says Horst Bettin, a chemist at the Physikalisch-Technische Bundesanstalt (PTB), Germany's national institute for weights and measures, in Berlin. If the IPK were damaged, its mass would be lower, and the definition of a kilogram—and that of a mole—would change as a result.



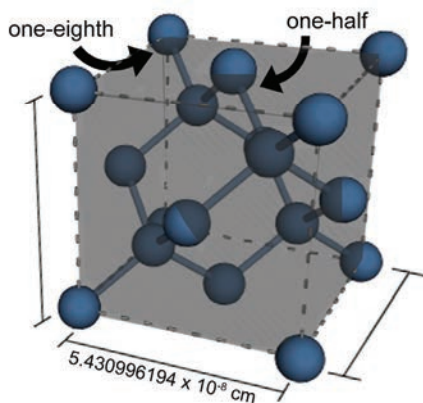
R. PRESS/NIST, GRAPHIC DESIGN: N. HANACEK/NIST

Just as the word “pair” means two and a “dozen” means 12, a mole of any given thing means there is roughly 6.022×10^{23} of it. These cubes show what one mole of aluminium, one of copper, and one of carbon look like.

$N_A = 6.022\,140\,857 \times 10^{23}$
 $h = 6.626\,070\,15 \times 10^{-34}$

Calculating the Avogadro Constant

Silicon (Si) crystallizes in an ordered lattice. This unit cell structure shows 18 atoms of Si. But only four of them are wholly inside the unit; six are on the faces of the cube, which means they are only halfway inside; and eight are at the corners, which are one-eighth inside the cube. That adds up to just 8 atoms inside one unit cell of the lattice.



Measured Si Properties in 2015

$$\text{Side length} = 5.430996194 \times 10^{-8} \text{ cm}$$

$$\text{Volume} = (\text{side length})^3 = (5.430996194 \times 10^{-8} \text{ cm})^3$$

$$\text{Density} = \frac{\text{sphere mass}}{\text{sphere volume}} = 2.320070960 \text{ g/cm}^3$$

$$\text{Molar mass} = 27.97697009 \text{ g/mol}$$

Based on the size of the unit cell, you can figure out how many atoms there are in a cubic centimeter, and based on the measurements of the silicon sphere, you can figure out how many moles there are per cubic centimeter:

$$\text{Atoms per cm}^3 = \frac{8 \text{ atoms}}{\text{volume of a unit cell}} = \frac{8 \text{ atoms}}{(5.430996194 \times 10^{-8} \text{ cm})^3} = 4.994033964 \times 10^{22} \text{ atoms/cm}^3$$

$$\text{Moles per cm}^3 = \frac{\text{density}}{\text{molar mass}} = \frac{2.320070960 \text{ g Si/cm}^3}{27.97697009 \text{ g Si/mol}} = 0.08292788506 \text{ mol / cm}^3$$

Given these two values, how would you calculate the Avogadro constant?

*The calculation is in the online Teacher's Guide at www.acs.org/chemmatters.

Chemist Robert Vocke at the U.S. National Institute of Standards and Technology worked with scientists around the world to redefine the mole.

Switching standards

The concept of a mole can be hard to grasp. In essence, the mole acts like an abbreviation for a gigantic number that enables scientists to convert enormous numbers of particles at the atomic level to quantities they can actually measure without having to shrink themselves down to the quantum realm like Antman.

Think about it this way: One molecule of water would be impossible for you to work with in the classroom. One mole of water, on the other hand, weighs 18 grams (the sum of the masses of a mole of oxygen atoms and two moles of hydrogen atoms). While not a huge quantity, 18 g is an amount (about 3.5 teaspoons) you can see and measure on a classroom scale.

Notice that you can determine a substance's molar mass (for example, 18 g for water) by expressing its atomic mass in grams. And you don't even need to know the value of the Avogadro constant to do so. But it's still useful for scientists.

How did scientists come up with the number of atoms or molecules in a mole? Over time, scientists' estimates of the Avogadro constant became increasingly precise. In the early 1900s, Albert Einstein used the Avogadro constant as it was

defined at the time in his doctoral thesis, which then led to a more refined estimate through later experiments by Jean Perrin.

Einstein had been investigating the movements of tiny particles, such as pollen, suspended in liquids. Perrin performed experiments to test whether Einstein's math was correct. In doing so, he refined the Avogadro constant estimate in 1908 to $5.7 \times 10^{23} \text{ mol}^{-1}$.

In the 1940s, further experiments would nail down the first 3 digits of the constant as 6.02, but the string of numbers that followed was questionable.

Silicon saves the day

The invention of X-ray instruments capable of measuring distances between atoms in a crystal led to the modern method for refining the Avogadro constant. With these incredibly precise measurements, scientists would be able to calculate the ratio of the volume of a mole of a crystal relative to the volume of a single unit cell of the crystal.

For this method to work, scientists needed an ideal crystal. It would have to be very pure with all of its atoms arranged perfectly in an ordered lattice, and have the same mass as the IPK, which at the time still defined the kilogram. The crystal would also need to be a sphere, because scientists would only need to measure its diameter to calculate volume.

In 1974, the U.S. National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, attempted the first modern measurement of the Avogadro constant on a natural silicon crystal. But natural silicon isn't pure—it contains three isotopes: ^{28}Si , ^{29}Si , and ^{30}Si , with about 92% ^{28}Si .

"This was the first direct measurement, but they also concluded at that time the next advance would come when you were dealing with enriched silicon," says Robert Vocke, a NIST mass spectroscopistW.

Creating the perfect silicon sphere

In 2004, the International Avogadro Coordination (IAC) was formed to create a pure silicon crystal. The effort began at the Central Design Bureau of Machine Building in Saint Petersburg, Russia, which had the centrifuges needed to produce enriched ^{28}Si . A centrifuge is an in-



⤴ A silicon sphere similar to this one was used to redefine the Avogadro constant.

strument that spins samples at high speeds to separate different substances or isotopes in a mixture. The lab produced numerous tiny crystals of 99.9995% ^{28}Si .

"Only one atom [in] 100 million was the wrong one," says Bettin.

The enriched ^{28}Si crystals then traveled to the Leibniz-Institut für Kristallzüchtung in Berlin, where they were melted and regrown as a cylindrical crystal weighing almost 5 kilograms (kg). That crystal went to the Australian Centre for Precision Optics in Sydney, where it was cut and polished into two 1-kg spheres.

Measurements of the spheres' diameters, the spacing between their atoms, and their densities fed into an equation that calculated the Avogadro constant. In 2015, IAC scientists published a result that met the requirements to redefine the mole with a relative uncertainty of 0.02 parts per million.

In November 2018, delegates from some 60 countries agreed to accept the new definitions of the kilogram and mole. The changes went into effect this year on World Metrology Day, May 20.

The kilogram is now defined in terms of the

Planck constant, which relates a photon's energy to its frequency. The mole now represents exactly $6.02214076 \times 10^{23}$ number of particles.

The change will be unnoticeable by most of us, but it signals a satisfying end of a centuries-long, global scientific quest.

XiaoZhi Lim is a science writer based in Boston, Mass.

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THE FUTURE OF FORENSICS

How past mistakes in forensics have transformed the field and defined its path forward

By Michael Tennesand

On July 26, 1978, John McCormick, a taxi driver in Washington, D.C., was ending his night shift when he was robbed and fatally shot outside his home. The victim's wife woke to the noise, and through her window, saw a lone assailant wearing a mask.

Evidence collected during the subsequent investigation pointed to 17-year-old Santae Tribble. An informant told police that Tribble was involved in the crime. An FBI examiner testified that a microscopic analysis of hairs found on a mask near the shooting matched Tribble's, and prosecu-

tors suggested to the jury that the chances the hair came from someone else were "1 in 10 million." Tribble maintained his innocence and passed a polygraph test. Three witnesses testified that on the night of the crime, Tribble was at his mother's apartment.

In January 1980, Tribble was sentenced to 20 years to life. In all likelihood, the microscopic analysis presented by the FBI forensics expert played a large role in persuading the jurors of Tribble's guilt. In 2012, he was exonerated based on another type of forensic evidence—DNA.



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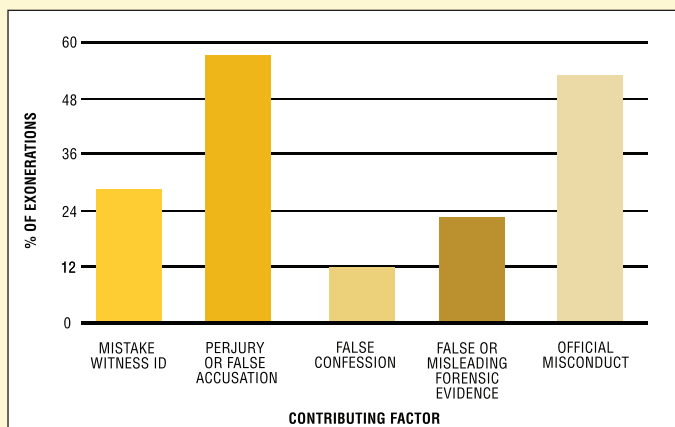
⤴ Fingerprint analysis isn't as reliable as it's often portrayed to be on television. One problem with the technique is that bias can affect whether an examiner matches a set of fingerprints to a suspect.



How the Wrong People End Up in Prison

Faulty forensics are undoubtedly a problem, but they are neither the only contributor to wrongful convictions, nor are they the largest contributor. Other factors, including false accusations and official misconduct, have also played significant roles in

the incarceration of innocent people, as shown in this graph. The chart includes known exonerations dating back to 1989. (Note that the percentages do not add up to 100%; this is because multiple factors can apply to any given case.)



KELSEY CASSELBURY, SOURCE: THE NATIONAL REGISTRY OF EXONERATIONS

Forensics and its flaws

Tragically, Tribble's story isn't unique. He is one of many who have been imprisoned for crimes they didn't commit. The reasons why this happens are complex. Flawed forensics is one piece of the puzzle.

The term **forensic science** includes the word **forensic**, which means argumentation or debate. **Science** is defined as the systematic study of the world through observation and experiment. These two words seem at odds with each other. But our judicial system is set up as a debate about the guilt or innocence of the accused. Law enforcement collects physical evidence for this process to form a picture of what took place at the crime scene and to support legal arguments for or against the conviction of a person on trial. Sometimes, a single piece of evidence—a hair, a bite mark—can make or break a case.

A critical approach to piecing together what happened at a crime scene uses a process that is likely very familiar to you: the **scientific method**. This classic foundation for a way of thinking about solving problems is at the heart of criminal investigations. Investigators begin with making observations at the scene of the crime. They collect and consider pieces of evidence. If there appears to be a connection between the evidence and the crime, they develop a hypothesis. To test their hypothesis, they run tests or collect further evidence.

But the scientific method has not always been diligently applied to forensics. In 2009, a seminal report on forensics released by the National Academies of Sciences (NAS)—a U.S. institution that analyzes issues related to science—concluded that “[w]ith the exception of nuclear DNA analysis, . . . no forensic method has been rigorously shown to have the capacity to consistently, and with a high degree of certainty, demonstrate a connection between evidence and a specific individual or source.”

The report listed the following methods as techniques lacking in scientific validation: bite-mark analysis, microscopic hair analysis, shoe-print comparisons, handwriting comparisons, firearms and tool-mark examinations, and fingerprint examinations—previously the gold standard of forensic analyses.

One of the issues that emerged from the report is the subjective nature of some of these traditional forensic methods. For example, research has demonstrated that information can bias a forensics specialist. One study showed that if fingerprint examiners were told that a suspect was in custody, they were more likely to match a fingerprint to the suspect. As recently as 2009, standardized rules for fingerprint examination simply didn't exist.

The overall lack of rigor for thoroughly validating forensic methods in the past has had profound consequences for Tribble and others like him.

Chemical Fingerprinting

What works

The good news is that the field of forensic science has come a long way. Today, even forensics students could probably have debunked the FBI hair analysis in Tribble's 1978 case. Hair without DNA is considered **class evidence**. Class evidence has characteristics common to a group of similar objects, but not one single object. For example, a blond hair discovered at a crime scene may point an investigator in the direction of a blond suspect. But even though a hair collected at a crime scene might share similar microscopic characteristics with hair from a suspect, the strand might not have come from the suspect.

In contrast, DNA evidence is categorized as **individual evidence**. This means that it can be linked to a specific, unique source.

Technological advances over the past three decades and the rigorous science behind DNA analysis has led it to become a benchmark for forensic evidence. DNA evidence has allowed law enforcement to establish more reliable connections between individuals and crime scenes. It has also been a key tool in exonerating hundreds of people who have been wrongly convicted, according to the Innocence Project, a legal network that helps prisoners fight charges against them.

In 2012, *The Washington Post* retold Tribble's story when he was exonerated of the murder he was accused of. Tests that year showed that DNA from the hair in the mask did not match Tribble's, despite the original microscopic analysis that concluded otherwise. A private lab even determined that one of the hairs found in the mask belonged to a dog. But by then, Tribble had already served time for a crime he didn't commit. On his release, Tribble had spent more years in prison than out. In 2016, a judge ordered the District of Columbia to pay Tribble \$13.2 million in damages.

In addition to DNA analysis, other reliable tools are available to law enforcement to aid them in investigations. **Gas chromatography** and **mass spectrometry** can identify chemicals such as drugs or other substances collected from a crime scene. Gas chromatography works by separating and analyzing compounds in a gaseous state. Mass spectrometry helps scientists identify molecules by measuring the mass-to-charge ratio of an ionized sample of a substance.

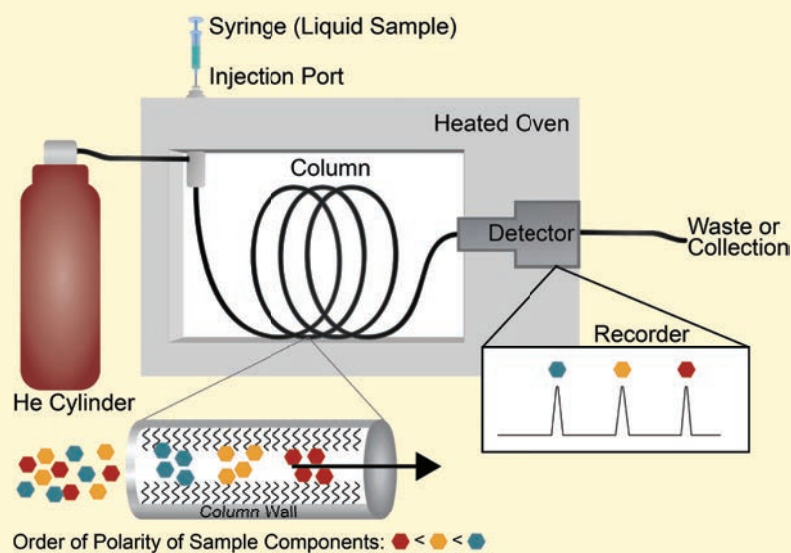
Crime labs can also use an instrument called a **Fourier transform infrared (FTIR) spectrophotometer**. FTIRs pass infrared radiation through samples, which can be solid, liquid, or gas. Some radiation is absorbed, stretching or bending bonds within a molecule. Some radiation passes through. The pattern of absorption and transmission is unique to a substance—a chemical fingerprint, so to speak.

At a crime scene, blood splatter, drugs, and other substances are often left behind, and it's not always obvious what's what. Identifying the various chemicals helps investigators figure out what may have happened.

Gas chromatography is one technique often used in forensic science to help positively identify the substances found at a crime scene. Here's how it works: A liquid sample is injected into a column, vapor-

ized, and carried by an inert gas, such as helium, through a column. The column contains a material called a stationary phase that slows down the flow of the sample's components based on their polarity.

As a component passes through and exits the column, a detector records the component's signal. Polar molecules bind more tightly to the stationary phase, and therefore flow through the column more slowly.



RACHEL PRIGER

The Jury Factor

Many people are generally familiar with some of the techniques used in crime detection, but applying the information may be subject to misconceptions or confusion. In a recent case, a juror objected to the use of a field test that indicated the suspect's car trunk was full of cocaine because the test was not performed in a "field." The juror was under the impression the test was only valid if done in a pasture or meadow, rather than on the street. Another jurist balked that a test was only 99% accurate, and did not seem to be beyond reasonable doubt in their mind.



GETTY IMAGES



Future of forensics

As for traditional forensic methods, researchers have tested and reviewed the limits of multiple techniques in response to the 2009 NAS report. In 2016, a follow-up report by the President's Council of Advisors on Science and Technology (PCAST) documented progress in forensic research. For example, scientists had studied the reliability of fingerprint analysis, and found that false positives were not uncommon, and examiner bias remained an issue. But recognizing that fingerprinting can still provide useful information, the PCAST report recommended that the technique's limitations be made clear to jurors for context.

Moving forward, the report further proposes that the scientific and law enforcement communities continue to work toward improved techniques to transform subjective methods into objective ones through research. Perhaps then, the reliability of these tests will help ensure that only the guilty are convicted.

Michael Tinnesand is a science writer and education consultant in Portland, Ore.

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Testing in the Field

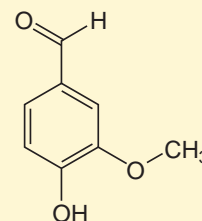
Police officers often use field tests to quickly determine whether someone is in possession of an illicit substance. Many of these field tests (quick analyses performed at a crime scene) involve a rapid color change that indicates the presence of a particular chemical compound.

Formaldehyde (CH_2O) and sulfuric acid (H_2SO_4) turn brown when applied to amphetamines and opium derivatives. Cobalt thiocyanate [$\text{Co}(\text{SCN})_2$] changes color in the presence of cocaine and barbiturates, and sodium nitroprusside ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$) is used to test for meth-amphetamines. The Duquenois-Levine (D-L) test, which involves vanillin ($\text{C}_8\text{H}_8\text{O}_3$), acetaldehyde ($\text{C}_2\text{H}_4\text{O}$), ethanol ($\text{C}_2\text{H}_6\text{O}$), hydrochloric acid (HCl), and chloroform (CHCl_3), is often used to screen a sample for marijuana.

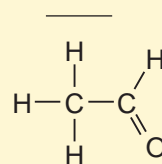
But field tests have limitations. A closer look at the D-L test demonstrates the reason for this.

Marijuana-containing plant material will develop a blue-purple color in reaction with the D-L reagent. No color indicates cannabinoids are not present in a sample. The test can't confirm, however, that a substance is definitely marijuana. Past studies on the field test have found that a variety of non-marijuana substances, including patchouli, cypress, and eucalyptus, yield positive results.

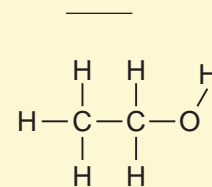
So, what a positive field test can't show is whether a substance in a person's possession is marijuana; it can only suggest that a substance might be. Because of this uncertainty, forensic labs have to run subsequent laboratory tests on samples of the same substance to confirm whether it's marijuana.



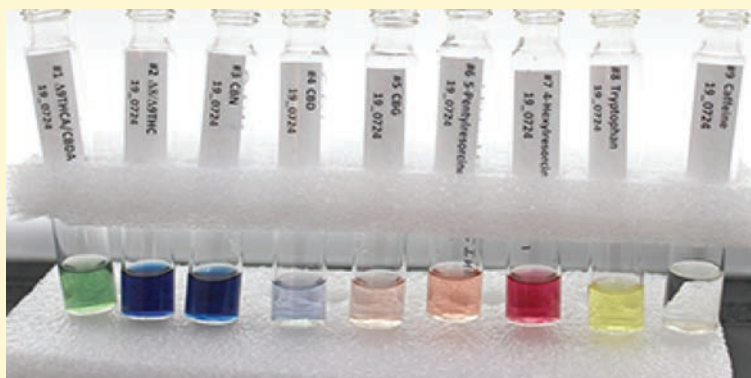
⌘ Vanillin, $\text{C}_8\text{H}_8\text{O}_3$



⌘ Acetaldehyde, $\text{C}_2\text{H}_4\text{O}$



⌘ Ethanol, $\text{C}_2\text{H}_6\text{O}$



⌘ Color-based tests are often used by law enforcement to determine whether someone is in possession of illicit substances. The D-L reagent (pictured), for example, changes color if a substance contains cannabinoids—but also other compounds not present in marijuana. Because the D-L test can yield false positives, forensic labs must run additional tests on a substance to confirm what is or is not in it.

Investigate the Career Path of a FORENSIC CHEMIST

In high school in Scottsdale, Arizona, Brandon Jones had his doubts about chemistry. His lab reports were mediocre, and he felt disorganized. But his teacher encouraged him to persevere.

“He really was the first person who got me into chemistry,” Jones says. His teacher was a huge CSI: Crime Scene Investigation fan, who made “all sorts of CSI jokes” and declared that his favorite compound was cesium iodide (CsI).

Whether it was through humor or something else, Jones’ teacher succeeded in interesting Jones in chemistry. After finishing high school, Jones earned a bachelor’s degree in chemistry from Arizona State University. He then went on to work at a quality-control vitamin company, where he ensured vitamin products met purity standards and matched the descriptions on product labels.

A year later, Jones started graduate school in forensic chemistry at American University in Washington, D.C. His graduate thesis was on synthetic cannabinoids, which were starting to become a problem around 2012, Jones says.

Synthetic cannabinoids are human-made chemicals that target the cannabinoid receptors in the brain. When sprayed on plants and smoked, synthetic cannabinoids can have a mind-altering effect similar to that of marijuana. People could legally sell the sprayed plants at that time, and research on them was sparse.

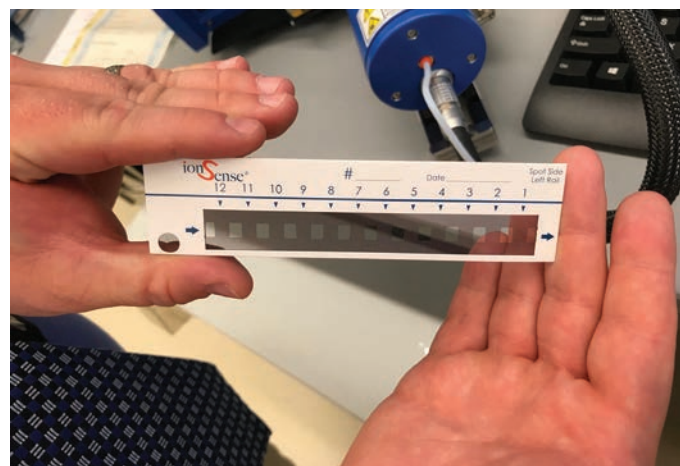
So Jones studied the substances in this emerging area, using gas chromatography-mass spectrometry (GC-MS). GC-MS is a method that can identify chemicals in a sample.

Jones struggled to find a job in forensics right after graduating, so he took a position as a substitute teacher.

Meanwhile, concerns over synthetic cannabinoids grew, and about a year later, Jones’ experience researching the drugs helped him land a position at Prince George’s County (Maryland) Drug Lab.

Jones is now working at the D.C. Department of Forensic Sciences (DFS), where he established a dedicated chemistry unit and develops new forensic techniques.

— Lis Gallegos and Raadhia Patwary



CHRISTINE SUH



CHRISTINE SUH

BRANDON JONES

B.S.: Chemistry, Arizona State University

M.S.: Forensic Science, American University

WHAT HE DOES NOW: Lead Chemist, D.C. Department of Forensic Sciences

What was the focus of your graduate research involving synthetic cannabinoids?

My research mostly involved developing a practical method to extract the synthetic cannabinoids off of different matrices (plants and liquids) and to analyze them using GC-MS.

When you started a new chemistry lab at DFS, what challenges did you face?

Doing it from scratch was a bit of a struggle. I went out to other forensic labs and talked to them about what kinds of problems they were dealing with. It’s all the behind-the-scenes stuff—working with other agencies to get stuff to us, having all the regulations set in place—that often becomes the hardest part.

What is one of your favorite parts of the job?

If we find something new such as an unknown drug, trying to figure out what it is is a lot of fun—it’s usually a little bit of a mystery to unravel.

How do you use your previous experiences to help you as a forensic chemist?

A lot of the aspects of teaching and tutoring come in handy when explaining forensic chemistry to attorneys. You have to break the chemistry down into much simpler terms.

What advice would you give to high school chemistry students?

If they know a place where they would want to work, just reach out. They’re usually happy to give tours or talks on what they’re doing, what kind of stuff they run... or at least allow you to shadow a chemist for a day. I know that it might seem intimidating, but all you have to do is reach out and ask.

Note: This interview was edited for length and clarity.

« Have you ever spotted a mysterious drop of liquid and wondered what it was? Equipment in forensic labs can rapidly reveal what is in a sample.



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