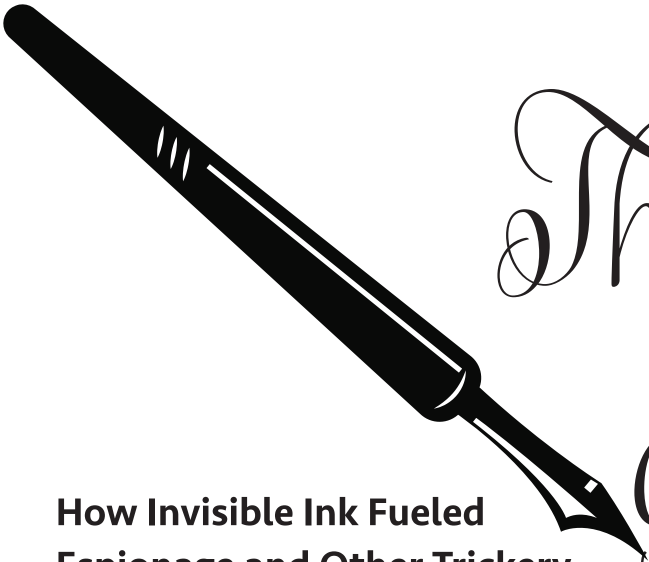


The Chemistry of Deception

How Invisible Ink Fueled Espionage and Other Trickery Throughout History

By Wynne Parry

In 1915, as World War I raged, British investigators searched the homes of two suspected German spies. In both cases, the British turned up incriminating evidence: pieces of lemons. During the trials that followed, the citrusy fruit provided key evidence against the spies, leading to their convictions, including a death sentence by firing squad for one.

If you've ever experimented with invisible ink, you might already know why those lemons caught the attention of the British. Write with lemon juice, and your message remains invisible until you heat the paper, then brown letters emerge.

Lemon juice ink was a surprising choice for a scientifically advanced nation such as Germany, writes Kristie Macrakis in her book, *Prisoners, Lovers and Spies: The Story of Invisible Ink from Herodotus to Al-Qaeda*.

Consisting only of juice, lemon ink is simple to make. The recipient of the secret message can make the ink appear merely by applying heat to it. Even at the time, most school children knew this trick.

Macrakis, however, notes that war intensifies the use of invisible ink and fosters the invention of new formulas. "There are more spies in wars and people need to communicate secretly in wars, as well," she says.

World War I was no exception. The Germans lost spies due to their use of lemon ink, which spurred them to develop harder-to-detect methods. Their innovations included the use of an invisible ink derived from a medical ointment that contained silver. This ink joined the numerous other invisible ink formulas that were devised over hundreds of years.

In the year 2 AD, the Roman poet Ovid made what is thought to be the first mention of invisible ink. In his book, *The Art of Love*, Ovid gave advice to love-struck Roman girls on how to sneak messages to their boyfriends. Ovid instructed them to write a message using fresh milk instead of ink. When the boy received it, he'd simply pour coal dust on the milky, hidden words, and they would show up.

The raw materials for some inks, such as fruit juices or human body fluids, are easy to get and turn into visible messages. Others, like the medical ointment or more modern recipes, require technical expertise. The secret to many of these inks, and their role in history, lies in their chemistry.

"MAGICAL WHITE INK"

During the American Revolution, the rebels used a different technology to send messages in secret. At first, a revolutionary spy operating among the British wrote his reports in regular black ink. But if these messages were intercepted, they could be read easily. That all changed when George Washington learned of a "magical white ink," Macrakis recounts.

Once on the page, this new ink, which was supplied by a patriot named James Jay, was invisible. It needed a specific reagent to make it visible. Washington realized that this would make it more secure, even if the note fell into enemy hands. It was more complicated to develop, and therefore harder to detect, than a simpler, heat-activated formula like lemon juice type inks, according to Macrakis' account.

A spy operating in New York City used the white ink to write his reports, which a chain of messengers transported across Long Island Sound to Washington's headquarters.

Galls are abnormal growths that result from infection, often by insects. Oak galls are rich in organic molecules known as tannins or tannic acids

DEPOSIT PHOTOS

Once developed with the reagent, these reports gave Washington valuable information about British movements. Washington never knew exactly how it worked, however, according to Macrakis.

An analysis more than 150 years later revealed that the ink was made of a tannic acid and developed with iron(II) sulfate ($FeSO_4$)—a formula that wasn't actually new. Similar types were used by military groups dating back to 300 BCE.

Oak galls, as well as other plants, produce an abundance of tannic acids, also called tannins. If you've had tea, coffee, chocolate, or other food and beverages that are naturally bitter, you've already had tannins, which have an astringent taste.

When combined, tannic acid and iron(II) sulfate interact to make a black ink. Anywhere from two to four tannic acid molecules wrap around the iron ion, explains Jason Lye, a color chemist who runs an innovation consulting company, Lyco Works Incorporated. When exposed to air the iron(II) ions oxidize to iron(III) ions, which produces a darker ink.

The process, in which organic molecules surround a metal atom by binding at multiple points, is known as chelation. It is also the basis for chelation therapy, which doctors use to capture heavy metals, such as lead, in the body and remove them.

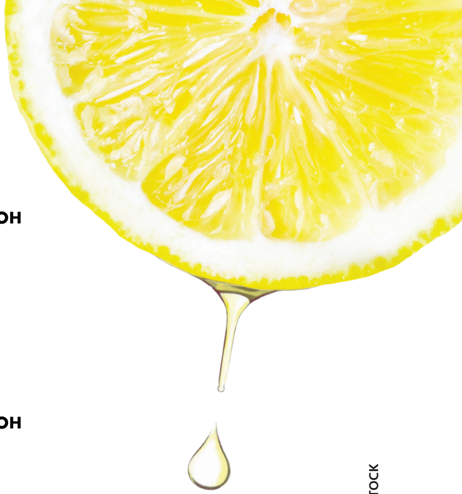
The term "tannins" describes a large group of related molecules, all of which contain aromatic rings with carbon atoms connected by resonating double bonds. These "double" bonds resonate with the "single bonds" and act more like a "one-and-a-half" bond, rather than "double" bond. These resonating bonds have energetic properties that affect the absorption of light and so contribute to the color our eyes perceive.

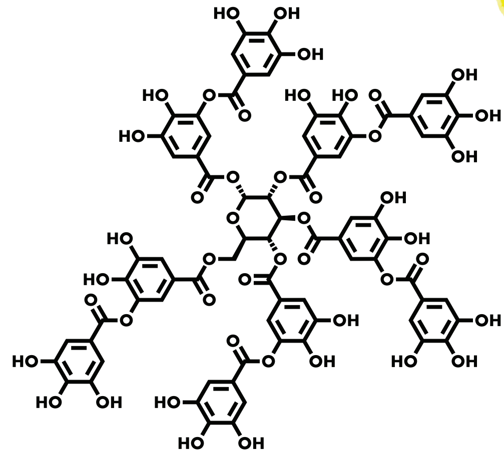
Tannic acid solutions are pale brown, like weak tea. When applied to paper lightly and allowed to dry, the writing is very difficult to see. But when the iron chelates are added to the tannins, the complex that forms is very highly colored, appearing dark blue or black.

LEMON JUICE INK

Like the white ink from oak gall, the lemon juice approach employed by the German spies also makes an effective invisible ink. A message is written on paper using liquid lemon juice. After the lemon juice dries, it is practically invisible. But why does it turn brown faster than the rest of the paper when heated, allowing us to read the secret message?

Both paper and lemon juice are complex mixtures composed of carbon linked to hydrogen, oxygen, nitrogen, and other select atoms. When heated, they begin to break down in the process of combustion. The process of





TANNIC ACID

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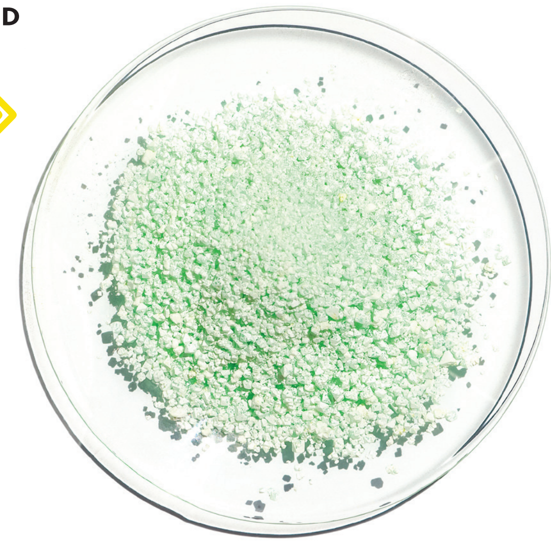
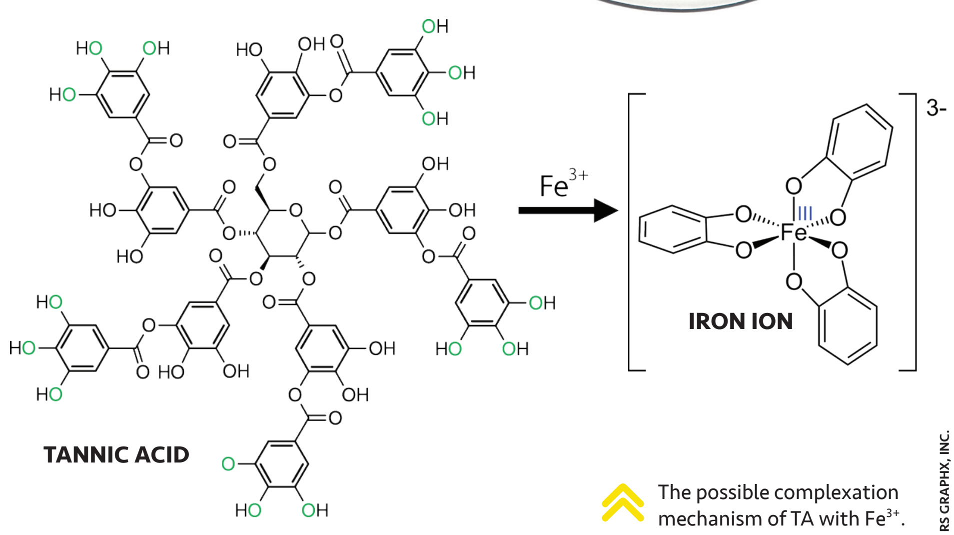
Iron (II) sulfate, also called green vitriol, made up half of the ink recipe used during the American Revolution. In crystalline form, iron (II) sulfate contains water molecules and has the full name iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$).]





TANNIC ACID

The possible complexation mechanism of TA with Fe^{3+}.

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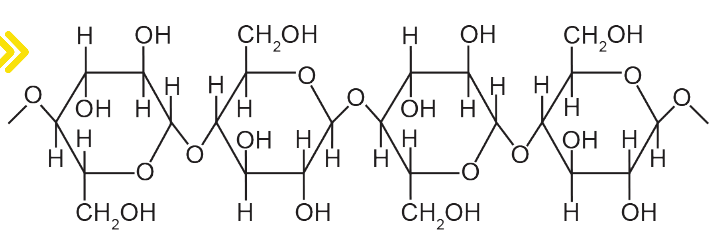
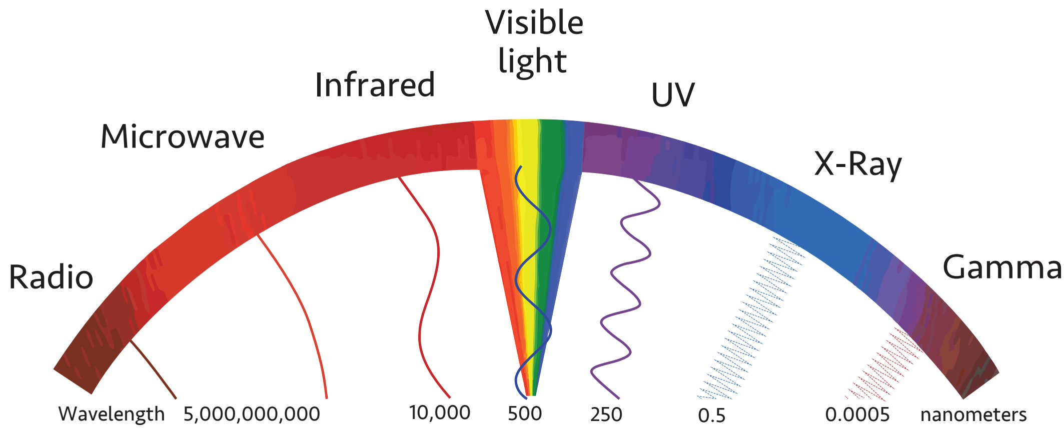
Cellulose molecules contain many sugar units strung together, making it a polysaccharide.





The human eye perceives color based on the wavelengths of light that a surface absorbs. Ultraviolet light, meanwhile, lies just outside the part of the spectrum that the human eye can detect.

combustion releases CO_2 and H_2O as the final products. But at low temperatures, the combustion may be incomplete and the carbon may show up as elemental carbon, which is black.

This reaction occurs faster in the dried lemon juice than in the cellulose molecules that make up the paper. Lemon juice contains simple sugars and acids that combust more rapidly. Cellulose is a complex polysaccharide that takes a bit more energy to react.

SILVER INVISIBLE INK

The simplicity of this reaction made it easy for the British to intercept their messages. So, the Germans stepped up their ink game.

Macrakis describes how German intelligence officers recruited a young American journalist to travel to Great Britain to gather intelligence. After the new recruit asked how his messages would pass undetected, the officers gave him the secret—a brown paste smeared on black, woolen socks. To write, he was to soak the socks in water, then use that solution as ink.

Although he confessed when the British apprehended him, the spy did not know how to develop the sock-paste ink. The British determined the brown substance was the antiseptic Argyrol, which contains colloidal silver dispersed within gelatin. The French, allies of the British, had also found socks containing a similar silver-based secret ink.

When the colloidal silver particles were applied the paper, they were too diluted to see. For years, it was a mystery as to the process that allowed the ink to be visible. It is this process that likely provided the basis for this invisible ink, according to Lye.

While the Germans' approach to developing these messages has been lost to time, Macrakis states that the French determined a way to make the writing visible. They put it in a development medium containing silver nitrate ($AgNO_3$) and a reducing agent, which is an electron donor. Then they passed an electrical current through the medium, a method called electrolysis.

Lye explains that the silver nitrate supplies additional Ag^+, which the electrolysis and the reducing agent turn to metallic silver (Ag) by transferring electrons to it. This metallic silver precipitates preferentially onto the existing silver atoms, slowly generating dark crystals where the spies had written.

ULTRAVIOLET INVISIBLE INKS

While many invisible inks rely on heat or chemical reactions to develop, another common form makes use of ultraviolet (UV) light. With its shorter wavelengths, UV light lies just outside the section of the electromagnetic spectrum that human eyes can perceive. Certain materials absorb the UV light then convert it to a longer, visible wavelength. This phenomenon is known as fluorescence.

A long list of surprising potential inks, including urine, semen, quinine (from tonic water), and some vitamins, can leave traces that stand out when under UV light. There are a number of UV markers available for home use. When a message is written on a piece of paper it quickly disappears. But when it is viewed under UV light, the message comes out in a fluorescent glow.

Apart from writing secret messages, these pens can also be used to mark private belongings so they bear the owner's name, with the idea that if they are stolen, the thief would not see the owner's name and wouldn't bother to remove it. If the item is recovered, a UV light will reveal the rightful owner.

While paper documents do remain important, a lot of today's communication no longer requires ink. Regardless, Macrakis doesn't seem worried about good old-fashioned invisible ink becoming obsolete. She jokes that when everyone is focusing on electronic communication, "that's the time to use invisible ink," she says. "It's less likely to arouse suspicion."

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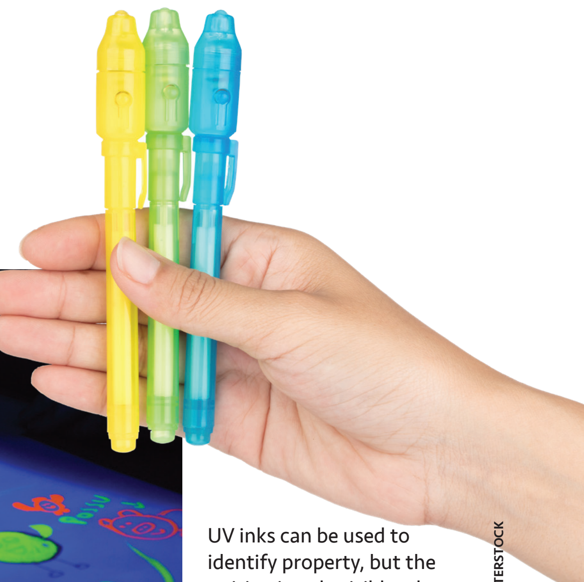

UV inks can be used to identify property, but the writing is only visible when exposed to uv light.

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