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MYSTERY MATTERS

Saint's Blood

by Robin meadows

On Saint Januarius's three feast days, what is alleged to be his centuries-old blood tranforms from a dark, clotted mass into a liquid. St. Januarius is the patron saint of Naples, and the miracle of liquefaction draws thousands of Roman Catholics to the Naples Cathedral to see a priest perform the rite. While the worshippers pray, shouting and invoking St. Januarius to liquefy his blood, the priest holds the vial of holy blood close to an altar bearing what is believed to be the remains of the saint's head. To check whether liquefaction has occurred—which can take from two minutes to more than two hours—the priest periodically turns the vial of blood upside down. When it flows, he announces, "The miracle has happened," and the crowd chants.

Some observers believe that there can be no natural explanation for the liquefaction of the blood, and it is truly a miracle. However, a number of scientists throughout history have suggested more worldly causes for the phenomenon. Recently, a team of Italian chemists simulated the liquefaction in the laboratory. Using their methods, a medieval alchemist could easily have created imitation blood that would solidify when undisturbed and liquefy when moved.

Thrown to the bears

The history of St. Januarius's blood is sketchy. Although little is known of the saint's life, legend has it that in the year 305 AD he and four other Christians were condemned to be thrown to the bears by the Romans, who had outlawed Christianity. But when the bears were put in the amphitheater, they refused to tough St. Januarius and his companions. So the Romans decapitated the martyrs instead. A serving woman named Eusebia collected St. Januarius's blood from the stone on which he had been beheaded, and gave the holy blood to the Bishop of Naples.

The blood is kept in an ornate reliquary (receptacle for sacred remains) topped by a crown and a cross. The reliquary encloses two airtight vials that contain the blood. One is narrow and contains only a few drops, and the other measures 10 centimeters and is about two-thirds full of a dark mass.

The reliquary is stored in a glass case in a guarded vault and is removed only for veneration on St. Januarius's feast days: the Saturday before the first Sunday in May, which is the feast of moving his remains to Naples; September 19, which is the feast of his martyrdom; and December 16, which is the feast honoring him as the patron saint of Naples.

Historical records of the liquefaction extend back many years, and there are at least 37 independent accounts of the phenomenon between 1389 and 1659. Prior to that time, however, the phenomenon is not well documented.

The first written notation of the liquefaction miracle was not recorded until 1389, more than 1000 years after St. Januarius's death. The 1389 record is in the diary of an anonymous citizen of Naples, who wrote, "...there was a great procession to mark the miracle wrought by our divine Lord with the blood of St. Januarius. The blood, which is kept in a vial, turned into liquid just as if it had been in the living body of Januarius on that very day."

Critics have drawn attention to two inconsistencies in the history of the vial of blood. First, one would expect a miraculous object to have a well-documented history, not to burst onto the scene in the 1300s. Second, the blood has liquefied at least seven times while jewelers were repairing the reliquary.

These anomalies can be resolved by the Italian chemists' explanation of the phenomenon. Luigi Garlaschelli, an organic chemist at the University of Pavia, and Franco Ramaccini and Sergio Della Sala, two colleagues in Milan, noticed that the relic behaved like a thixotropic gel. Such gels can liquefy when picked up, shaken, or otherwise disturbed mechanically, and then resolidify when left to stand. Examples of thixotropic gels include some types of mayonnaise, which can be liquefied instantly by shaking or stirring, and toothpaste, which oozes when squeezed from the tube yet does not drip off the toothbrush. The simple act of inverting the reliquary containing St. Januarius's blood would be enough to liquefy some thixotropic gels.

Garlaschelli traveled to Naples to witness the ceremony and said that the vial of blood "is very dark—maybe darker than our gel. It looks more like strong coffee than like blood, and it doesn't show any red hue and leaves on the walls of the bottle a thin yellow-brown layer." His observation of the color is significant because blood—at least fresh blood—leaves a distinctly scarlet color on the walls of a glass container.

Garlaschelli and his colleagues simulated St. Januarius's blood, first by dissolving iron(III) chloride, $FeCl_3$, and calcium carbonate, $CaCO_3$, in distilled water. The two salts reacted to form red-brown iron(III) hydroxide, $Fe(OH)_3$. The next step was purifying the iron(III) hydroxide solution by removing the unreacted iron(III) chloride and the calcium chloride, $CaCl_2$, a reaction byproduct.

The chemists removed these salts by dialysis, which entails putting the solution inside a membrane sac with pores that let small compounds (such as the salts) out while keeping larger compounds (such as the iron(III) hydroxide) in. The membrane sac is then put in distilled water, and the salts flow out through the membrane until the concentrations inside and outside the sac are equal. The chemists changed the distilled water daily until it no longer turned yellow from iron(III) ion, which took three to four days.

Just as salts flow out of the dialysis membrane, water flows in and so increases the volume of the iron(III) hydroxide solution. To concentrate the solution, the chemists put it in a crystallization dish until about half the water had evaporated. Finally, they added sodium chloride, NaCl, which resulted in a dark, brownish thixotropic gel that set in about an hour. The gel was easily liquefied by gentle shaking. The liquefied iron(III) hydroxide gel left a thin, yellow-brown layer on the walls of the glass container—similar to what Garlaschelli observed when the blood of St. Januarius was liquefied in Naples.

Medieval reagents

Most of the techniques used by the Italian chemists—using a balance, distillation, and crystallization—were known in the 1300s. Dialysis, however, is not documented as having been known until the early 1600s, when it was shown that salt could pass through a bladder. But dyes were stored in bladders and gut bags in the 1300s, and it is entirely possible that an alchemist living then could have discovered dialysis. Garlaschelli and his colleagues showed that their technique works when gut is used for the dialysis bag.

Likewise, the three compounds used to simulate St. Januarius's blood were readily available to medieval alchemists living in the vicinity of Naples. Two of the compounds were widely available in the

1300s: calcium carbonate was obtained from a variety of sources, including chalk (limestone) or finely crushed eggshells, and sodium chloride was obtained from rock salt or sea salt.

The only source of the third compound, iron(III) chloride, during that time was a mineral called molysite, which occurs naturally only near active volcanoes; molysite precipitates out of lava when hydrochloric acid comes into contact with iron-containing rocks. Interestingly, Naples is near Mount Vesuvius, a 1190-meter active volcano. Moreover, after St. Januarius's blood miraculously liquefied in the 1300s, a number of similar miracles occurred in or around Naples.

These geographical and temporal coincidences suggest that a medieval alchemist may have concocted what is believed to be St. Januarius's blood. Many medieval priests were also gifted alchemists. Unfortunately for them, in 1317 Pope John XXII forbade the study of alchemy, saying, "Alchemists deceive us and promise what they cannot perform... if any members of the clergy are found among alchemists they will receive no mercy."

This restriction might have led to the following scenario: Excited by his discovery of the thixotropic properties of molysite mixed with chalk, and denied any other way of sharing his excitement, a priest/alchemist may have presented his finding as St. Januarius's blood on one of the three feast days. As Garlaschelli and his colleagues point out, even if this scenario is correct, modern priests who perform the rite of liquefying St. Januarius's blood are not cheating when they invert the reliquary; this is the only way they can ascertain whether the miracle has occurred.

Closed vials...open questions

The chemists' simulation does not disprove the claim that St. Januarius's blood has liquefied, and it certainly does not prove that the vial contains a gel made from iron(III) chloride and calcium carbonate. Indeed, other researchers have suggested that the vial could contain real blood mixed with a thixotropic honey such as that from heather, a shrub with small pinkish flowers. However, Garlaschelli's work shows that neither blood nor a miracle is necessary for making a dark brown solid liquefy on command.

The mystery of the composition of St. Januarius's blood will probably never be solved, because the Catholic Church will not allow analysis of the substance in the vial. However, as Garlaschelli and his colleagues wrote in a report of their work, "Our replication of the phenomenon seems to render this sacrifice unnecessary."

Make a blood-like thixotropic mixture

In 15.0 mL of distilled water, dissolve 15.0 g of iron(III) chloride hexahydrate, $FeCl_3 \bullet 6H_2O$. The compound dissolves to form ions,

$$FeCl_3 \bullet 6H_2O(s) \Rightarrow Fe^{3+}(aq) + 3Cl^{-}(aq) + 6H_2O(l)$$

and the Fe^{3+} ion reacts with water to form a yellow, acidic solution

$$Fe^{3+}(aq) + H_2O(l) \Rightarrow FeOH^{2+}(aq) + H^{+}(aq)$$

This is the first of a series of three reversible (equilibrium) steps in which Fe^{3+} can react with water. Slowly add 4.0 g of powdered calcium carbonate, $CaCO_3$, while stirring. The mixture will foam from the production of CO_2 gas as some of the acid is neutralized.

$$CaCO_3 + 2H^{+}(aq) \Rightarrow CO_2 + Ca^{2+}(aq) + H_2O(l)$$

This reaction consumes H^+ and therefore causes the $FeOH^{2+}$+ in the second reaction to react further with water (in two additional reactions, summarized in one equation below). The dark brown product consists of very small (colloidal) particles of $Fe(OH)_3$.

$$FeOH^{2+}(aq) + 2H_2O(l) \Rightarrow Fe(OH)_3(s) + 2H^{+}(aq)$$

Pour some of the solution into a small bottle with a screw-on top, add a tiny amount (200 crystals) of table salt, NaCl, cap and shake the bottle. Let the bottle stand for 24 hours, then tilt it gently to see if it has gelled. If it has not, add more salt and repeat the test after 24 hours. If it appears solid try shaking it to see if it will liquefy. If it won't, open the bottle, add 10 drops of water, shake, and repeat the test after 24 hours.

This chemical system lends itself to many experiments. You may wish to divide your sample into two equal portions before adding the salt, keep one as a control, and add salt (half the amount specified above) to the other. It is possible to compare the gel obtained from laboratory-grade calcium carbonate with the gel formed when you substitute a medieval source of the compound—finely ground egg shells.

The gel produced by this formulation is not especially stable and may precipitate after a few days. Detailed instructions for using dialysis to make a stable blood-like gel are in the current issue of the *Chem Matters Classroom Guide*. (David Robson).

CAPTIONS

In Naples, Italy, a bishop tips an ornate reliquary that contains a glass case. Inside are two glass vials of a yellow-brown substance said to be the 1600-year-old blood of Saint Januarius.

An artist's depiction of Saint Januarius, emphasizing the miraculous claims about his blood. Using artistic license to put different parts of the story into one image, the artist shows Saint Januarius holding what appear to be two vials of his own blood. Volcanic Mount Vesuvius, in the background, may have been the source of the mineral molysite that could have been used to prepare imitation blood.

Chemists Sergio Della Sala, Franco Ramaccini, and Luigi Garlaschelli cooperated on the laboratory investigation of simulated blood. They were unable to examine the sample that is alleged to be the blood of Saint Januarius, but they prepared an iron-based gel that seems to have the same physical properties.

BIOGRAPHY

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