

Nevertheless, preliminary research suggests that the outlook for laser cooling larger molecules is good. Theory groups led by Anna Krylov, Svetlana Kotochigova, and Anastassia Alexandrova have analyzed the vibrational structures of many candidate molecules, and they predict that coolable molecules can incorporate some rather large organic structures, including benzene rings.⁵ On the experimental side, Doyle and colleagues have already done transverse in-beam cooling of calcium monomethoxide (CaOCH_3), although they still have a long way to go before they can catch that molecule in a trap.⁶

Cooling larger molecules would introduce even more richness to cold-molecule experiments. For example, if researchers could cool a molecule that breaks mirror symmetry, they could investigate whether the laws of physics treat such asymmetric molecules differently from their mirror-image counterparts. More broadly, by bringing all the well-known power of chemistry to bear on the ultracold regime, researchers could design ultracold molecules with shapes and properties to suit any purpose. “We don’t know whether our techniques are as broadly applicable as that,” says Doyle. “That’s a frontier scientific question.

We’re very interested in seeing what’s possible.”

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X-ray imaging shows how a 17th-century painting lost its color

When an arsenic sulfide pigment chemically degraded, it stripped the painting’s yellow rose of visible details.

As beautiful as they are to look at, art masterpieces are not eternal. For example, pigments and binders in oil paintings inexorably degrade. Light, humidity, and temperature fluctuations are the usual culprits, but exposure to certain cleaning solvents during conservation and the mixing of incompatible pigments by the artist can also render paint unstable over time.

The task of conservation scientists is to understand the chemical reactions that cause the degradation in order to answer three questions: How was the painting made, how did it originally appear, and how did it change—either naturally or by intervention? Those questions are not entirely backward-looking. By reconstructing how a painting deteriorates, conservators may be able to forestall further damage and better preserve it.

Paintings conservator and doctoral student Nouchka De Keyser (Rijksmuseum, University of Amsterdam, and University of Antwerp), her advisers Katrien Keune and Koen Janssens, and their colleagues have scientifically addressed all three questions in their analysis of a yellow rose in Abraham Mignon’s mid-17th-century painting *Still Life with Flowers and a Watch*,¹ shown in figure 1. Mignon painted his yellow roses with the mineral orpiment (As_2S_3), used by artists



FIGURE 1. STILL LIFE WITH FLOWERS AND A WATCH (left), by Abraham Mignon, oil on canvas (c. 1660–79), Rijksmuseum. **(a)** In its current form, the central yellow rose appears flat and lifeless. **(b)** The map of arsenic distribution reveals the element’s presence throughout the rose and Mignon’s original painted details. X-ray powder diffraction identifies the arsenic in the form of transparent lead arsenates rather than the original yellow-orange mineral orpiment (arsenic sulfide). (Adapted from ref. 1.)

since antiquity to give a bright and vibrant appearance. But orpiment can be problematic. Over time, the mineral can severely discolor, changing the look of painted orange draperies, lemons, yellow flowers, and golden metal in old masterworks.

Many artists, possibly including Mi-

gnon, were aware of those and the mineral’s other problems—it dries poorly, is incompatible with other pigments, and is extremely toxic. Yet it remained widely used until the 18th century. And orpiment was not the only troublesome pigment. In Vincent van Gogh’s 1888 painting *The Bedroom*, for instance, the fading

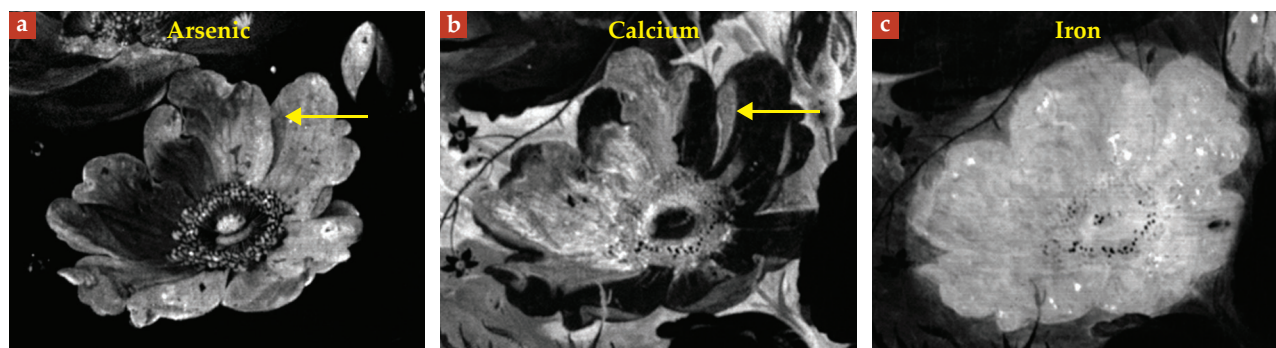


FIGURE 2. X-RAY FLUORESCENCE maps. **(a)** The distribution of arsenic in the paint reveals detailed features on the petals and stamens and how the rose would have looked when illuminated from the upper left. **(b)** The distribution of calcium correlates with the shadows cast by upper flower petals on a neighboring petal (marked by the yellow arrows). **(c)** In the iron distribution map, only the rough shape of the flower is visible. From comparisons with powder-diffraction maps of the area, the iron signal stems from a more uniformly applied ochre underpainting beneath the flower. (Adapted from ref. 1.)

of red pigments turned its purple walls blue and its pink floor brown. De Keyser and her colleagues wanted to understand what happened in the case of Mignon's yellow rose. "The most interesting part of my job," she says, "is to play detective, look for evidence of specific chemical reactions, and retrace their steps to figure out what an artist really had in mind."

Chemical analyses

Most of the flowers in Mignon's painting remain brilliant. But the rose stands out as flat, monochrome, and peppered with microcracks. De Keyser and her colleagues first analyzed the rose using x-ray fluorescence imaging. When an x ray shines on the surface, it can knock out a core electron from an atom in the paint. That electron emission, in turn, prompts an outer valence electron to drop from a higher to a lower orbital and fluoresce. The light's wavelength is characteristic of chemical elements in the paint layers that absorbed the x rays. And when the x-ray beam and photon detector are raster scanned over the painting, the resulting image reveals the spatial distribution of those elements.

The researchers mapped the locations of arsenic, calcium, iron, sulfur, lead, and copper in the area containing the rose. Surprisingly, the analysis revealed painterly features—light and shadows defining the petals and stamens—that are optically invisible in the rose's now-degraded image (figure 1a). But because the elements still reside there, albeit in different molecular form, the arsenic map of their microscale distribution (figure 1b) uncovers the rose in most of its former glory. To compare

specific element distributions, see figure 2.

X-ray fluorescence cannot, however, resolve specific chemical compounds, into which orpiment transformed over the centuries. So the group turned to x-ray diffraction. Because pigments were originally ground into powders to make the paint mixture, the randomly oriented grains in Mignon's canvas allowed the researchers to avoid alignment difficulties associated with single-crystal diffraction. Indeed, obtaining molecular specificity from powder diffraction is becoming an increasingly key technique to study old paintings.²

To resolve molecular structures at the painting's surface, the group used an instrument developed in Janssens's lab at the University of Antwerp. In reflection mode, x rays strike the paint surface at a shallow 10° angle. De Keyser and her colleagues raster scanned the instrument across the area of the rose in 1.5-millimeter steps with 10-second exposure times per pixel. Altogether, the scan took 13 hours.

Those powder-diffraction maps primarily identified two lead arsenates—schultenite (PbHAsO_4) and mimetite [$\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$]. The reactions leading to them start with the photooxidation of orpiment into arsenolite (As_2O_3), a semi-soluble molecule that can diffuse throughout the multilayered paint system. When the oxide comes across lead ions, subsequent reactions prompt the precipitation of schultenite and mimetite. Each of them has a distinct spatial distribution in the painting.

The transparent and the visible

Schultenite and mimetite lack the bright yellow appearance of orpiment; rather,

they're colorless and pale-yellow crystals, respectively. And when blended with calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and quartz (SiO_2)—other minerals that are identified by powder diffraction and whose refractive indexes match that of oil—the yellow paint used to create the rose becomes virtually transparent. Crystals of orpiment still exist in the painting, but only along the border of the rose. The pigment's early prevalence is now gone, chemically transformed into largely transparent crystals.

The fluorescence map bears out the result. Iron is pervasive over the surface of the rose, and the diffraction map identifies it in the form of goethite, a key ingredient in yellow ochre. Like other 17th-century still-life painters, Mignon is thought to have adopted a multistep method. He first blocked out the position of the flowers with a monochrome, ochre-based underpainting and then built up the details by applying glazes for shadows and orpiment for sunlit parts.

In that approach, he marked the location of the rose using the inexpensive ochre. Indeed, because the original orpiment has faded into transparency, the ochre underpaint is now the only optically visible remnant. The modern rose looks dull, flat, and monochrome—the opposite of what Mignon would have intended.

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