

St Luke's new coat

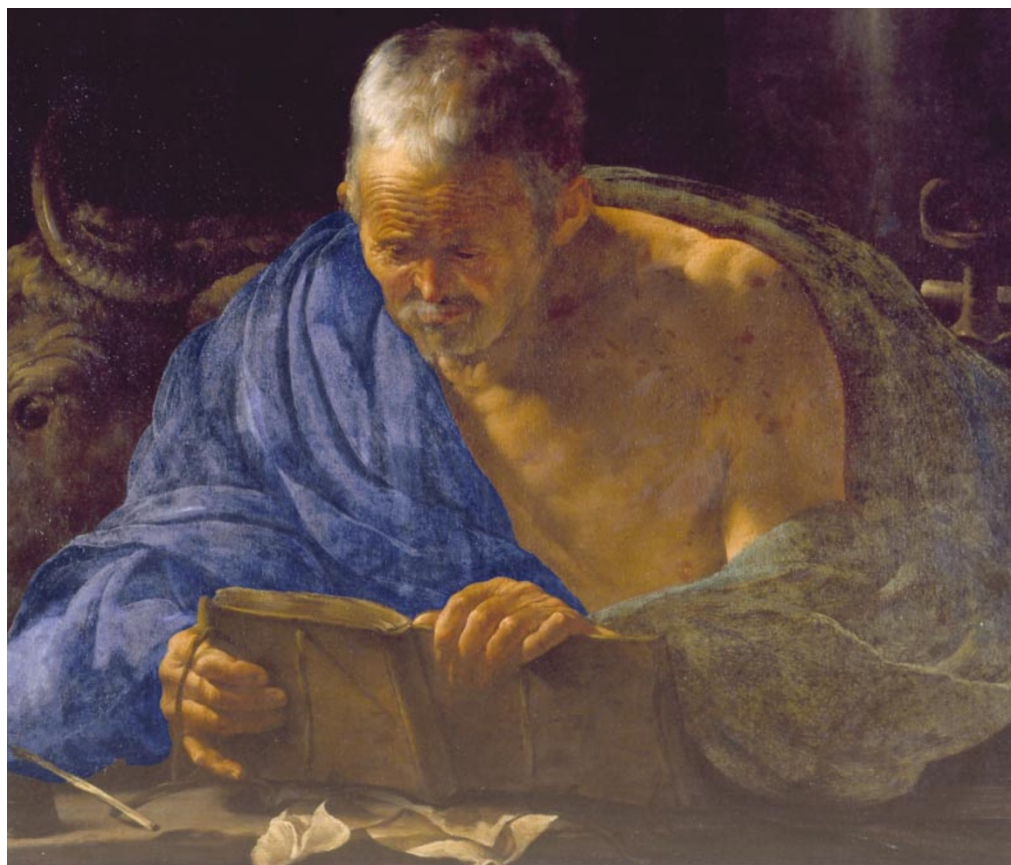
By combining chemical analyses with digital image reconstruction, it is possible to complete virtual restorations of deteriorated paintings. Celeste Bieber considers the technology's potential.

When the Dutch master Hendrick ter Brugghen embarked on his *Four Evangelists*, a series of paintings that depict the authors of the New Testament, he gave each a different-coloured cloak, or mantle. Little did he know that the blue pigment he chose for St Luke's garment would not stand the test of time.

Painted in 1621, the four artworks reside in the Deventer Municipal Museum in the Netherlands. Whereas the mantles of Matthew, Mark and John are still resplendent in evocatively textured shades of yellow, red and green, respectively, Luke's cloak has long since faded to a dull and flat grey. But now Dutch researchers led by Joris Dik, a chemist at the University of Amsterdam, have produced a likeness of the original using a technique called autoradiography, combined with digital image reconstruction.

Digital reconstructions of artworks based on chemical analyses are still rare, and Dik's is the first to be achieved without any destructive sampling of the painting. Although there is still some controversy among art historians as to the validity of such techniques, some are now starting to sit up and take notice. "The possibility of digital restoration is interesting," says Martin Kemp, an art historian at the University of Oxford, UK, and a regular contributor to *Nature's Science in Culture* column.

St Luke's mantle faded because ter Brugghen used the 'smalt' pigment, a crushed, potassium-enriched glass containing silicon, oxygen, arsenic and cobalt — the latter of



Feeling blue: Hendrick ter Brugghen's St Luke from the *Four Evangelists*, seen here with one half of his mantle in its current faded state and the other in digitally reconstructed splendour.

which imparts a deep blue colour. It was favoured by artists throughout the sixteenth, seventeenth and eighteenth centuries as a cheaper, synthetic alternative to ultramarine. The latter was made from a brilliant blue mineral called lapis lazuli that had to be imported from Afghanistan.

Although art historians have known that smalt fades over time, the chemistry involved has only recently become clear. "It is difficult to get at the reaction mechanism," explains Dik. "Although it may have dramatic optical consequences, the chemical change is small."

But last year, researchers led by Jaap Boon, an analytical chemist at the Institute for Atomic and Molecular Physics in Amsterdam, showed that the fading of smalt is due to the leaching of potassium ions from the glass¹. Boon argues that the presence of potassium ions in the smalt glass encourages a tetrahedral arrangement of oxygen ions around each cobalt ion. Cobalt ions can absorb a specific amount of energy to boost an electron to a higher energy level. When the oxygen ions are in a tetrahedral coordination, this corresponds to the energy of red and green light,

so this is absorbed, leaving blue light to be reflected.

But when the soluble potassium ions leach out, smaller protons replace them. Without the potassium to enforce the tetrahedral coordination, the oxygen ions surrounding each cobalt ion arrange themselves octahedrally instead, altering the amount of energy that the cobalt can absorb. This energy no longer corresponds to visible light, and the blue colour is not selectively reflected.

Colour coordination

Although they lose their ability to create colour, the cobalt ions, and traces of arsenic, remain in the ground glass. And it was by detecting their presence that Dik and his colleagues were able to attempt their reconstruction, giving a quantitative indication of where and how intense ter Brugghen intended the blue colour to be.

Dik's team put the painting in a nuclear reactor for 10 minutes to bombard it with neutrons. A tiny proportion of the cobalt and arsenic nuclei were able to capture neutrons and become unstable, radioactive isotopes — cobalt-60 and arsenic-76. These then decayed to stable, non-radioactive nickel-60 and selenium-76, respectively, by emitting β - and γ -radiation.

Radioactive arsenic-76 has a half-life of just over 24 hours. The day after irradiation it was therefore the major emitter and so



Joris Dik: revealing artists' true colours.



In the pink: Campaña's *The Conversion of the Magdalen* before (top) and after reconstruction.

the researchers placed a photographic film against the radioactive painting for two and a half hours to obtain a density map. Cobalt-60 has a much longer half-life, so the team applied a separate film after 10 days and left it in place for 4 months. Combining the films gave a two-tone map of where, and how intensely, cobalt and arsenic were originally applied to the painting in the smalt. The photographic films show "precisely every brush stroke", says Dik.

Hidden talents

Autoradiography has been used on paintings since the 1970s, mainly to gain insight into artists' working methods. Scientists at the Metropolitan Museum of Art in New York, for instance, have used the method to reveal Rembrandt's use of different palettes for separate sections of his paintings², and have discovered a hidden self-portrait beneath Anthony Van Dyck's *Saint Rosalie Interceding for the Plague-stricken of Palermo*². Dik's new twist is to use his autoradiographs to complete a digital reconstruction.

Dik mixed his own smalt paint according to seventeenth-century recipes. Reflectance spectroscopy of this paint allowed computer software to reproduce the colour and combine it with the two-tone radiographic mappings. Dik superimposed the resulting blue mask on a digital scan of the original painting to give the final reconstruction³.

Other experts in the chemistry of art are

intrigued by the results, although there is a lively debate about the accuracy of Dik's reconstruction. "This method is very interesting because it is the first time a digital technique has been used quantitatively," says David Saunders of the scientific department at the National Gallery in London. "However, there is one snag. It is not necessarily correct to assume the intensity of colour to be proportional to the concentrations of cobalt and arsenic."

Dik agrees, but explains that this simplification is unavoidable. The radiation signal comes from the entire paint layer but the colour you see when you look at a painting comes mainly from the upper sections. This could explain why Ernst van de Wetering, an art historian at the University of Amsterdam, finds Dik's approximation of the mantle colour too "garish".

Other groups have also recently attempted digital reconstructions. Saunders' department, for instance, has produced a reconstruction of Pedro Campaña's *The Conversion of the Magdalen*, which dates from the latter half of the sixteenth century. As a result of the instability of the red lake, smalt and green verdigris pigments, the balance of colour and some of the intended meaning has been lost. For example, Christ no longer seems to be the focus of the painting because his robe has faded from a strong pink to a pale one.

Saunders and his colleagues took pinprick-sized samples from the painting and

studied the individual pigment grains under a microscope. By supplementing this with non-intrusive, microscopic analysis, peering through cracks in the paint to deduce the layer structure, they were able to identify the pigments used and assess their relative proportions. The team then mixed their own paints according to the results of the analyses, determined their colours, and then used the results to restore the painting digitally⁴.

On the spot

But the problem with taking measurements on spot samples is that the resulting reconstruction is based on the assumption that the samples' composition is representative of a much larger area. "You have no idea how representative a sample is," says Thomas Learner, a conservation scientist at Tate Britain in London. Saunders agrees, and adds that Dik's approach has further appeal because some paintings are too precious to subject to destructive sampling. "There are some paintings that we would deeply love to sample that we wouldn't dream of attacking," he says.

Learner laments that his team cannot emulate Dik's work because he lacks the funds to gain access to a research reactor. Indeed, Dutch scientists are leading the way at the interface between chemistry and art, not least because of an initiative called MOLART, backed by the NWO, the Netherlands Organization for Scientific Research. Since 1995, more than 70 scientists interested in art, including Boon, have worked to understand the molecular basis of ageing in paintings. Their work has been funded to the tune of 7 million guilders (US\$2.9 million), mostly by the NWO. "They are my biggest competitor," jokes Dik, whose work was supported by the Nuclear Research Group in Petten and by the Amsterdam branch of Christie's auction house.

Despite the efforts of MOLART and Dik's group, some experts believe that many art historians still aren't fully aware of what science can offer. "There is still a tendency among art historians to assume that what they see now is what the artist painted," says Joyce Townsend, a senior conservation scientist at Tate Britain.

Dik and his colleagues hope that digital reconstructions will help to raise awareness of the contribution that chemistry can make, and have plans to analyse about 10 more paintings. "Autoradiography is a great tool," says Dik. "It means you can do digital reconstruction in a much more scientifically verifiable way." ■

Celeste Biever is currently studying journalism at City University in London.

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2. Ainsworth, M. W. (ed.) *Art and Autoradiography: Insights into the Genesis of Paintings by Rembrandt, van Dyck, and Vermeer* (Metropolitan Mus. Art, New York, 1982).
3. Dik, J. et al. *Z. Kunsttechnol. Konserv.* (in the press).
4. Richardson, C., Saunders, D. & Spring, M. *Z. Kunsttechnol. Konserv.* 15, 338–346 (2001).