ETH zürich

## TAILOR-MADE MEDICINE

Shaping the healthcare of tomorrow PAGE 12

Board game brings deforestation to life PAGE 8 On the trail of the Zurich Mona Lisa PAGE 38 The architect of public transport PAGE 46

# Looking for clues to the origins of Zurich Mona Lisa



The Laboratory of Ion Beam Physics is one of the world's leading groups in the dating of organic materials. As well as analysing fragments of clothing worn by Ötzi the Iceman, the team has also worked on pigments from Mona Lisa paintings.

TEXT Samuel Schlaefli IMAGE Daniel Winkler

he first thing that catches your eye is the solid wooden frame and gold-leaf finish. Shift your gaze to the subject of the painting and you see the pale, gentle face of a young woman with her hands crossed, sitting in front of a panoramic river landscape. Could that really be Mona Lisa, Leonardo da Vinci's masterpiece, reputedly insured for 800 million dollars?

It's a chilly Thursday morning in Zurich's Kreis 5 district, and we have arranged to meet doctoral student Laura Hendriks at the Welti-Furrer warehouse, which stores artworks from all over the world under secure, temperature-controlled conditions. The Zurich Mona Lisa on the table in front of us belongs to a Swedish private collector who purchased it from a Japanese businessman. Otherwise, little is known about its real origins. That means we could potentially be looking at a previously unknown second painting of Mona Lisa by da Vinci himself! Experts are still divided as to whether he painted multiple versions of his famous portrait in the 15th century – but that's exactly what Hendriks hopes to find out.

Two men wearing white cloth gloves skilfully remove the poplar-panel painting from its opulent frame. Hendriks leans over the portrait and scans it with a UV light, discussing what she sees with Irena Hajdas, her doctoral advisor. Dark patches appear as if by magic, indicating that the painting was retouched at some point in the past. Hendriks marks two points on the woman's hand and sleeve using coloured stickers. Then she puts on a pair of special glasses, with a monocular lens over the right eve, and starts searching the marked areas for fine cracks in the original paint. Using a sharp, razor-thin needle, she extracts two tiny pigments from an existing crack, carefully choosing a spot that will have the least impact on the painting. She places the paint samples between two small sheets of glass – and visibly relaxes. "Quite a topic I've chosen for my doctoral thesis, don't you think?" she asks merrily.

Applying half-life methods to dating Hendriks has developed a highprecision method of dating artworks by measuring the carbon in the binders

Stickers mark the spots where samples are to be taken for radiocarbon dating.





## "Quite a topic I've chosen for my doctoral thesis, don't you think?"

Laura Hendriks

used in oil paints. Having qualified as a chemist, she subsequently opted to do her doctorate in a lab run by Hans-Arno Synal, ETH Professor and Head of the Laboratory of Ion Beam Physics. His group is one of the world's leading laboratories in the field of radiocarbon dating, the same method that Hendriks is applying to determine the age of the Zurich Mona Lisa. Radiocarbon dating - also referred to as carbon-14 dating – was first developed in the 1940s, when the American physical chemist Willard Frank Libby hit upon the ingenious idea of using the rate of decay of the unstable <sup>14</sup>C isotope to measure the age of organic material. All living things ingest <sup>14</sup>C continuously. As a result, the concentration of <sup>14</sup>C is approximately the same in both the biosphere and the atmosphere. As soon as an organism dies, however, the <sup>14</sup>C begins to decay, with a half-life of 5,700 years. The carbon isotopes <sup>13</sup>C and <sup>12</sup>C, on the other hand, don't decay. Consequently, researchers can compare the concentrations of the  $\rightarrow$ 

different isotopes to determine how much time has passed since the <sup>14</sup>C began to decay. Modern radiocarbon dating techniques can be used to determine the age of bone, wood and paper samples up to 13,000 years old. Since the concentration of <sup>14</sup>C in the atmosphere varies from one century to the next, scientists have been calibrating radiocarbon measurements since the 1980s by counting the number of growth rings in old trees, a science known as dendrochronology. To acquire this data, Synal works closely with the Swiss Federal Institute for Forest, Snow and Landscape Research (WSL). Radiocarbon dating can even be extended back as far as 50,000 years by calibrating the measurements using data on ocean sediments.

Sophisticated measuring technique The tricky task of measuring the tiny and extremely rare <sup>14</sup>C isotope requires the use of a highly sophisticated physical measuring technique known as accelerator mass spectrometry, or AMS. Some of the world's most accurate accelerator mass spectrometers are in the basement of the HPK, the oldest research building on ETH Zurich's Hönggerberg campus. Up to 10 metres long, they are composed of polished chromium-steel tubes, vacuum pumps, ion sources, particle accelerators, Faraday cages, solenoids and detectors. All the spectrometers in the HPK building were developed by Synal's 35-strong team. In 2013, he and colleagues founded the spin-off Ionplus to market the products they were developing. Today, over 20 of these AMS systems – which can cost up to 3 million Swiss francs each – are up and running worldwide.

On a visit to the underground laboratory, which is the size of a sports hall and has metre-thick concrete walls, Synal explains how radiocarbon dating works. First, the sample - a pigment from the Zurich Mona Lisa, for instance – is subjected to chemical pretreatment to remove any contamination that could interfere with the results. What remains is converted into carbon dioxide in a combustion process at around 2,000 °C, and then reduced with hydrogen. The result is an ultra-thin carbon layer in a small test tube. It contains scarcely a milligram of carbon, but that's enough to



Accelerator mass spectrometer on the Hönggerberg campus



"Sometimes our research is a bit like detective work."

Hans-Arno Synal

analyse it using AMS. This is remarkable, considering that the <sup>14</sup>C isotope is extremely rare – occurring in a sample only about as frequently as a single grain in a two-cubic-metre block of sand. Having prepared the sample, the next step is to use a particle accelerator to separate the remaining carbon into its tiniest particles. At the end of this complex process, only the <sup>14</sup>C isotopes reach the detector in the spectrometer. The system counts them and compares the result with the proportions of <sup>12</sup>C and <sup>13</sup>C, which are determined in subsequent measurements. The resulting ratio is used to calculate the radiocarbon age, which can then be converted to an absolute calendar age by consulting the dendrochronological calibration curve.

### The Turin Shroud and the Charter

Synal's Group has already carried out a number of groundbreaking studies, including a project in 1988 to determine the age of the Turin Shroud. Many Christians believe that Jesus was

wrapped in this burial cloth after his crucifixion. However, the lab's analysis put the linen cloth's age at 676 years,  $\pm 24$  years, a result that was backed up by carbon dating results from the universities of Oxford and Arizona. This ruled out the possibility that the Turin Shroud was authentic. In 1991, the laboratory dated the founding document of the Swiss Confederation: the Federal Charter, or Bundesbrief. Some historians had begun to question the claim that the document actually stemmed from the year 1291. Using radiocarbon dating, Synal was able to prove that the paper and ink were, in fact, 700 years old,  $\pm 35$  years. His group has also worked on a piece of clothing from the frozen mummified corpse of Ötzi the Iceman. This sample is stored at -16°C in a small Schott flask in a chest at the laboratory.

"Sometimes our research is a bit like detective work," says the professor. A few weeks ago, Synal was asked to analyse a piece of canvas he received in the post from the Düsseldorf museum that houses the art collection of North Rhine-Westphalia – but he was given no information on the sample's origins. Shortly after sending the <sup>14</sup>C dating results to the client, he heard on the news that a Malevich painting at the museum had been exposed as a forgery. In addition, art and antique dealers have tried to misuse Synal's analyses to prove the authenticity of works and drive up their prices, a practice he emphatically rejects: "Radiocarbon dating is precisely that: a method of dating things, not proving their authenticity. We can tell you when something was produced with a high degree of precision, but not whether something is genuine or fake."

#### Radiocarbon age from pigment

So how about the Zurich Mona Lisa at the fine-art storage facility? Could it

really have been painted by Leonardo da Vinci himself? There is still no conclusive answer to that question. The results of a previous radiocarbon dating study showed that the oil painting's poplar panel dates from the 15th century, which coincides with da Vinci's career as an artist. However, an x-ray examination revealed that the Mona Lisa was painted over a previous portrait of a male figure. Meanwhile, Laura Hendriks' analyses indicate that the blue pigment used in the painting was produced after 1830, though it remains unclear whether the pigments came from the original paint or from paint applied during subsequent restoration work. Each new analysis enriches the pool of information that art historians can draw on to evaluate the authenticity of the work.

In any case, Hendriks is pleased with the samples she took at the art storage facility. Her results clearly demonstrate that the analysis of paint binders is an effective way of preventing researchers from being led astray by old, reused wooden panels and canvases. "It's fascinating to use a combination of methods from physics and chemistry to gradually unearth the origins of artworks," she says. Hendriks can imagine continuing her radiocarbon detective work in a museum once she finishes her doctorate: perhaps even in the Louvre, home to the bona fide Mona Lisa. Dozens of researchers are engaged in analysing and dating the Louvre's world-famous collections - and they even have their own ion accelerator to help them get the job done.  $\bigcirc$ 

Laboratory of Ion Beam Physics:  $\rightarrow$  <u>www.ams.ethz.ch</u>