Paint sample analysis with 3D synchrotron X-ray microtomography

Ester Ferreira

With its research into 3D synchrotron X-ray microtomography, SIK-ISEA has entered virgin territory and helped to expand our understanding of chemical decay in layers of paint.

In 2007 the art technology department began to examine the early paintings of Cuno Amiet (1868–1961). In addition to his studio practice, work processes and materials, they studied the changes that can occasionally be observed on the surface of Amiet's paintings and the underlying processes of chemical decay.

To explore these complex analytic questions, tiny samples of material are removed from a suitable point on the painting. The typical diameter of these samples is less than 500 micrometres, which means that they are usually smaller than the full stops in this text. The established approach adopted by art technologists when analysing samples of material from paintings is to choose between two techniques: one-dimensional (for bulk analysis) or two-dimensional (for imaging). One-dimensional chemical analysis allows us to describe the composition of the sample with considerable accuracy. But to understand the size, shape and distribution of components within the sample in their original context, we need a second dimension so that we can generate a plane. To this end, the material is embedded and a slice is examined in cross-section under large magnification. Combining the one- and two-dimensional techniques is extremely instructive and has become the standard procedure.

However, for our analyses of highly complex degradation processes, the distribution, size and shape of the components did not seem to be adequately represented by a single slice of a sample.[1] When in 2006 the Villigen-based Paul Scherrer Institute (PSI) made its Synchrotron Swiss Light Source available to external researchers, we decided to try out non-destructive 3D synchrotron X-ray microtomography, a procedure hitherto unknown in the field of

art technology, with the aim of accessing the third dimension. We suspected that this would let us extract information from our tiny material samples that would not be available from the conventional procedures of art technology.

Electrically charged particles emit light as they traverse a curved trajectory. In the PSI's synchrotron light source, electrons move at velocities approaching the speed of light along a circular path with a circumference of 288 metres. A total of 350 magnets repeatedly focus the electron beam, keeping it on its curved trajectory, while acceleration cavities ensure that it maintains its speed. The synchrotron light is emitted at a tangent to the trajectory. At 21 points around the circumference, there are "beamlines", where researchers use light emitted by the synchrotron to analyse the properties of different materials. One of them, the TOMCAT beamline (Tomographic Microscopy and Coherent Radiology Experiments), is the basis for 3D synchrotron X-ray microtomography (Ill. 1).

To benefit from the PSI's analytical equipment, applicants must submit a research plan, which then has to be approved by an external panel of experts. Successful applicants are allocated specific sessions, when they can use the device and also benefit from technical support. In SIK-ISEA's Annual Report for 2007, we reported on our pioneer study (pp.76–78), which passed the application process and was successfully completed in August of that year. This gave us our initial experience with applying microtomography to paint samples. Since then, together with the Amsterdam-based natural scientist Prof. Jaap Boon, we have put together three more applications to continue the study and have accordingly been granted access time by the PSI. In two cases we have already taken up the option. By now our pioneer study has developed into a robust research project, playing an important part in the Art Technology Focus Project "Painting in the Early 20th Century". The third, recently approved session at the PSI will be taken up in 2010 and will advance our research even further.

The aforementioned expert Prof. Jaap Boon works for the Institute for Atomic and Molecular Physics (AMOLF) in Amsterdam, which is part of the Foundation for Fundamental Research on Matter (FOM). He has made a name for himself though two Dutch research programmes[2] in the field of art technology. These were carried out between 1995 and 2006 and dedicated to a molecular study of the technology and degradation of paints used historically by artists, and they have spawned numerous dissertations as well as a series of major publications. Our informal cooperation with Jaap Boon over the past two years, while testing samples with 3D synchrotron X-ray microtomography, is to be formalised as a part-time contract from 2010 until the end of the project. This way he will be able to inject vital momentum into the research on a continuous basis. Furthermore, his laboratory in Amsterdam will provide us with access to crucial specialised equipment for treating the surface of our samples.

To conduct a microtomographic examination, the material is taken straight from the painting without any pre-treatment and affixed to the point of a pin (Ill. 4). Synchrotron radiation is used to derive high-definition X-rays of the sample, and after each exposure the pin with the sample is turned by a fraction of a degree until it has rotated 180°. These two-dimensional image data are then combined into a three-dimensional model of the entire sample, which accurately displays differences in material density to a maximum resolution of 350 nanometres (0.000350 millimetres). With the help of specialised software, we can examine the tomographic sample not only from all sides, but even from the inside on any chosen cross-section (Ills. 8 and 9). It is only during subsequent chemical analysis that the original sample is in any way manipulated, and by referring to the virtual model we can now target a suitable slice for specific treatment. The results of these analyses help us, in turn, to interpret the three-dimensional image. In the course of our work so far we have gradually become aware of the potential offered by 3D synchrotron X-ray microtomography

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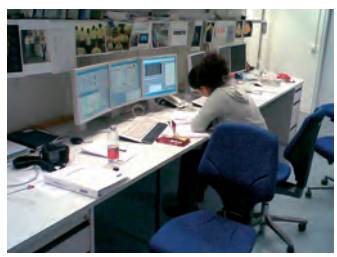
Ill. 1
Outside view of the TOMCAT beamline, Synchrotron Swiss Light Source (SLS) in the Paul Scherrer Institute (PSI), Villigen.

Ill. 2
Dr Ester Ferreira in the beamline control centre.

Ill. 3
Prof. Jaap Boon at the beamline.



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for understanding the internal structure of paint layers and the way they decay. The following case study will illustrate this potential.

The object of our examination was the primer under the painting *Winter in Oschwand* (1907) by Cuno Amiet (Ill. 5). The primer is easily visible where the canvas is stretched around the edges and has not been painted over. It is white, consists of multiple layers and its surface reveals numerous tiny, protruding lumps (Ills. 6 and 7) which, we suspected, had formed internally. To discover more about this phenomenon and its consequences for the painting's stability, we wanted to study the composition, size and shape of the lumps and also their distribution within the foundation layer in relation to fissures formed by drying and to the fibres of the canvas. A sample was taken from the primer on the left edge. Microtomography at the PSI was followed by chemical analyses in our own laboratory. This revealed that the binding agent was oil and the pigment was alkaline lead carbonate (white lead) with the

addition of small amounts of barium sulphate and zinc sulphide (lithopone) as well as a clay mineral. We furthermore identified aggregates of lead carboxylates, also known as lead soap, that in all likelihood were formed by a reaction between the hydrolysed oil binder and the white lead. These soaps are relatively mobile within a layer of primer or paint. They can, as seems to be the case in the primer examined here, combine into aggregates and migrate to the surface of the layer. Thanks to X-ray microtomography, where they appear as darkened areas due to their high X-ray permeance (Ill. 9, red arrows), we can now reconstruct their distribution throughout the entire sample. By dying them we can highlight them visually and compare their location even better with the lumps and micro-fissures on the surface of the sample (Ills. 10 and 11). In this example, the comparison showed that some of the lumps which can be seen on the surface are, indeed, lead soap aggregates. Examination of the primer also suggested that there is a relationship between lead soap aggregates and micro-fissures. The hypothesis formulated on the basis of these results – that a soap aggregate represents a weakness in the layer, which in turn is a starting point for the formation of fissures – must be tested in the course of further study.

Our initial tests demonstrated that dense anorganic pigments and fillers and less dense binding agents and products of degradation can be usefully contrasted using 3D synchrotron X-ray microtomography and represented to an accuracy of 350 nanometres. Even samples containing lead, like the one discussed above, which require extremely high radiation energy (38 keV), can produce significant tomographies. Specific components and voids can be localised. The shape of the soap aggregates can be visualised and observed in a spatial relationship to canvas fibres and micro-fissures, which in turn permits conclusions about the mechanism behind the genesis of the soaps, their migration patterns and how these processes affect the stability of the painting.

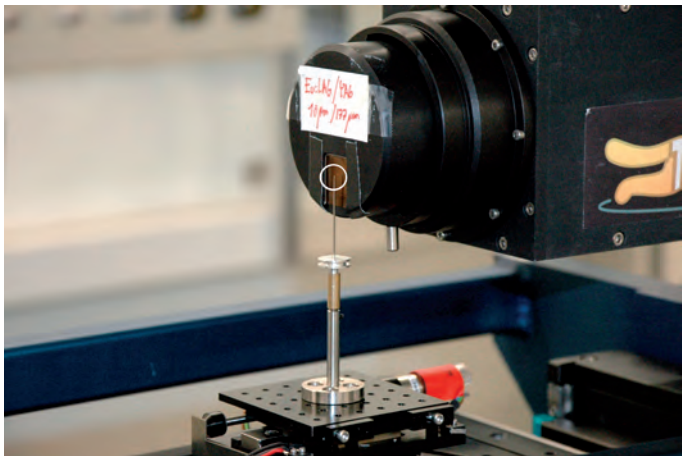
Up till now we have examined approximately 20 individual samples in this manner. Some preliminary results have already been published.[3] Findings have likewise been presented at various international expert conferences in the fields of art technology, conservation science and optics, where they have met with an excellent response.[4] The further course of this innovative research project is being watched with some excitement by professionals in the fields of art technology and conservation science.

1 Ester S. B. Ferreira, Jaap J. Boon, Jerre van der Horst, Nadim C. Scherrer, Federica Marone and Marco Stampanoni, "3D Synchrotron X-ray Microtomography of Paint Samples", in: *O3A: Optics for Arts, Architecture and Archaeology II,* edited by Luca Pezzati and Renzo Salimbeni, Proceedings of SPIE Vol. 7391 (SPIE, Bellingham, WA, 2009), 72910L-1.

2 The research programmes "MOLART" (1995–2002) and "De Mayerne" (2001–2006) by the Netherlands Organisation for Scientific Research (NWO).

3 Ester S. B. Ferreira et al., 2009 (see note 1).

4 *Picture Meeting* at the Instituut Collectie Nederland (ICN) in Amsterdam (April 2009); International conference on Non-destructive and Microanalytical Techniques in Art and Cultural Heritage (TECHNART) in Athens (April 2009); annual meeting of the international *Society of Photographic Instrumentation Engineers (SPIE Europe)* on *Optics for Arts, Architecture and Archaeology* (O3A) in Munich (June 2009); Interdisciplinary Symposium on 3D Microscopy (SSOM) in Interlaken (July 2009); *Studying Old Master Paintings - Technology and Practice,* Conference at the National Gallery in London (September 2009).



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Ill. 4
The sample (identified by a white circle) on its specially designed holder.

Ill. 5
Cuno Amiet, *Winter in Oschwand,* 1907, oil-based paint on primed canvas, 60.5 x 54.5 cm, privately owned.

Ill. 6
Excerpt from *Winter in Oschwand*, centre left. On the far left, the primed canvas is tacked to the stretcher bar, and the sample shown was taken from this edge.

Ill. 7
Detail of the primed canvas edge of *Winter in Oschwand* under large magnification. Numerous little lumps are visible on the surface. The smallest unit of the scale on the photograph is 100 micrometres (1/10 millimetre). The sample measures 10–50 micrometres.

Ill. 8
3D X-ray tomographical model of the sample. Once processed by the specialised software, the inside can be viewed on any cross-section.

Ill. 9
The sample can be virtually sliced in any direction and at any angle. The xz, yz and xy slices shown here correspond to the cross-sections in Ill. 8. The distribution of lead soap aggregates is easily recognised (red arrows).

Ill. 10
The sample surface: the red lines indicate micro-fissures in the layer.

Ill. 11
Spatial proximity is illustrated by the colour-marked lead soap aggregates (yellow) and micro-fissures (red), suggesting that the aggregates triggered the formation of the cracks.

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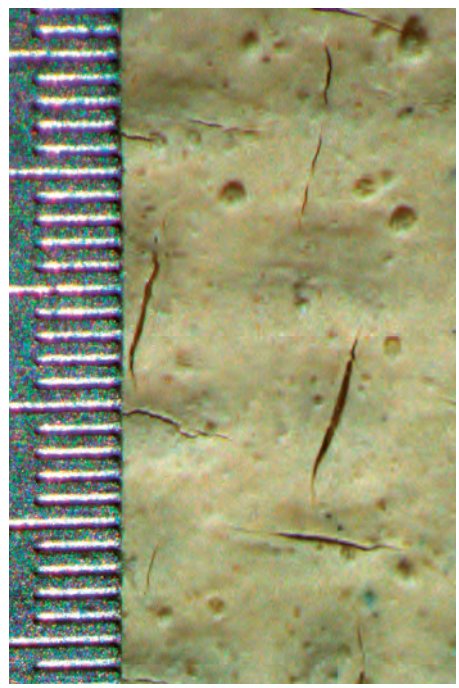

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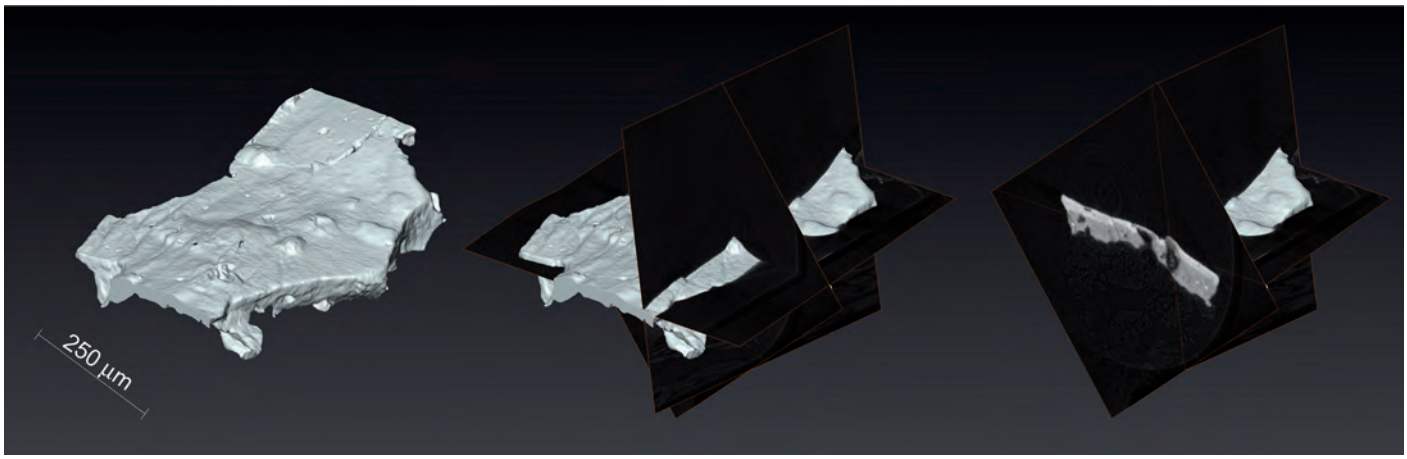

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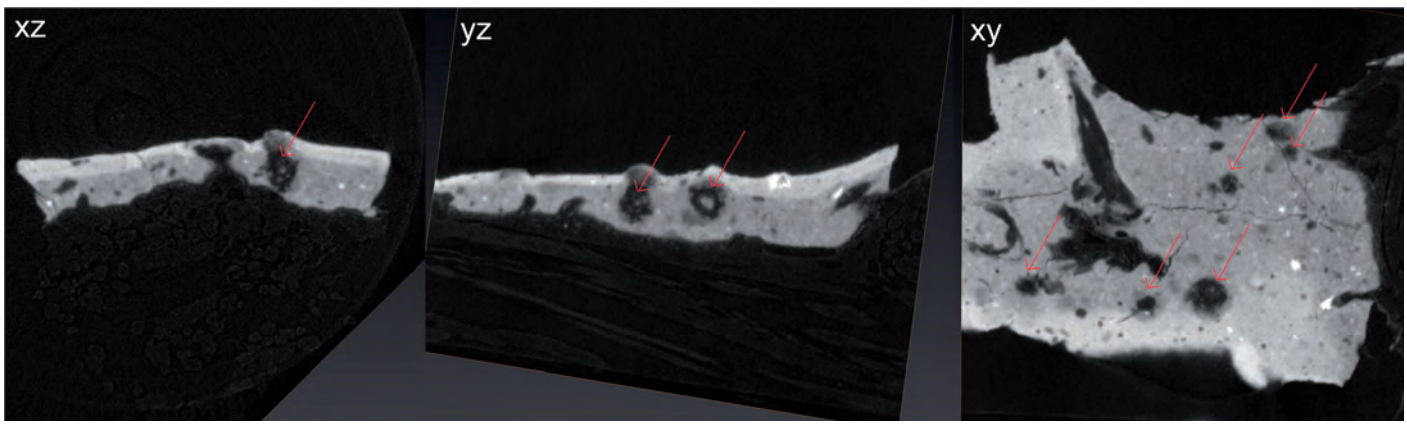

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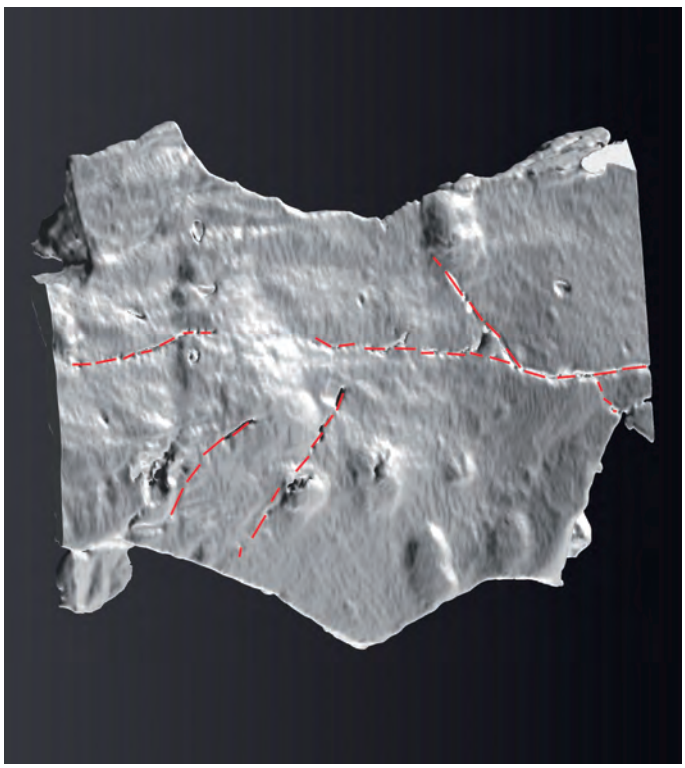

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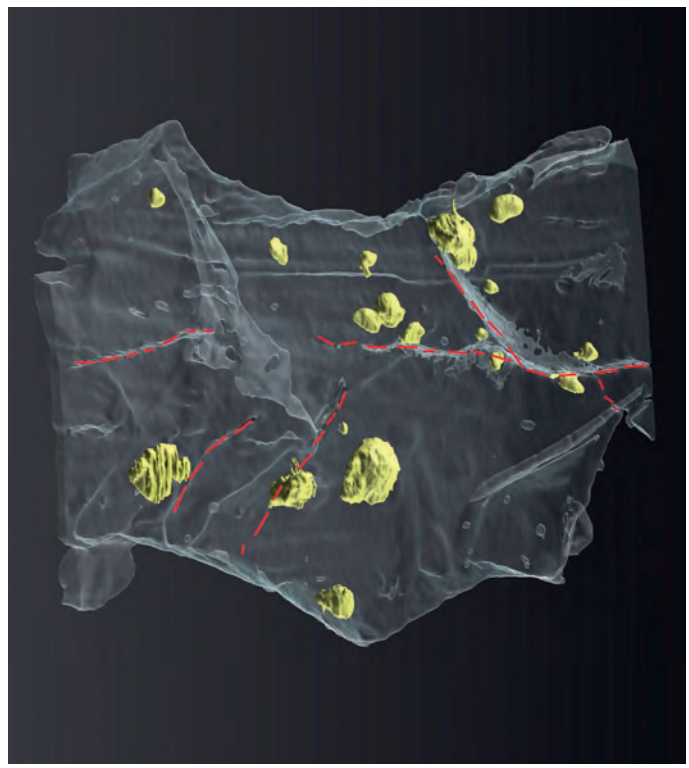

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