THE EXAMINATION OF PAINTINGS BY REMBRANDT WITH NEUTRON AUTORADIOGRAPHY AND A COMPARISON OF NEUTRON AUTORADIOGRAPHY WITH SCANNING MACRO-XRF

Art historical background

The questions of art historians and conservators concerning the genesis of the composition, the way of paint application and the condition of the painting can be answered with various radiation techniques of the whole surface of the painting.
For the reproduction of paint layers below the visible surface infrared reflectography\(^1\), X-ray radiography\(^2\) and neutron autoradiography (see below) are well suited. For a comprehensive evaluation, all three are necessary; none can replace one of the other methods. Autoradiography and X-ray radiography complement one another. The latter illustrates the distribution mainly of lead-containing pigments, which are not visible in autoradiography. Autoradiography adds information of paint layers coloured with other pigments. The autoradiography method is described

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Fig. 1  Circle of Rembrandt, »Man with the Golden Helmet«, Berlin, Gemäldegalerie. – (Photo J. P. Anders).

Fig. 2  X-ray film. – (X-ray G. Schulz).
in detail in another paper in this issue (Denker/Lau-
renze-Landsberg, this volume).
For this reason, the Gemäldegalerie is very lucky that
the information of neutron autoradiography can be
added to that of the X-radiograph, which is pro-
duced by the technical photographer in the Museum.

Paintings by Rembrandt

»Man with the Golden Helmet«

30 years ago there were rumours that the Rem-
brandt Research Project in the Netherlands intended
to definitively withdraw the attribution to Rem-
brandt of one of the most famous paintings by Rem-
brandt, the »Man with the Golden Helmet« (fig. 1)
in the Gemäldegalerie Berlin. By examining the
painting with neutron autoradiography the Gemäl-
degalerie had been able to take over the controver-
sial ascription into its own hands.
In the X-ray film (fig. 2) we see one of the reasons
why the authorship of Rembrandt was doubted. In
the face, there is hardly any absorption by the pig-
ment white lead. This is very untypical for Rembrandt
who has formed his faces with a thick application of
paint mixed with white lead.
In 1994 the »Man with the Golden Helmet« was
activated. At that time, the research reactor was
equipped with a large thermal column. The neutron
flux of \(1 \times 10^7\) n/cm\(^2\)s was too low to cause an
activity sufficient to produce well-darkened autora-
diographs. However, the neutron flux could be
enhanced to \(6 \times 10^7\) n/cm\(^2\)s by removing part of the
graphite. Furthermore, the darkening of the films

Fig. 3  3rd autoradiograph, film exposure 1d-4d after the end of
activation, contributing isotopes \(^{64}\text{Cu}, \(^{76}\text{As}\). – (Autoradiograph

Fig. 4  5th autoradiograph, film exposure 11d-23d after the end
of activation, contributing isotopes \(^{32}\text{P}, \(^{60}\text{Co}\). – (Autoradiograph
was increased by a factor of four by using intensifying screens during film exposure. The examination confirmed the existing suspicions (figs 3-4). The detected brushstroke is of a slow and hesitant manner, leaving blobs of colour, and is not at all compatible with that of Rembrandt’s temperament found by our investigation in secured works. An auxiliary line that marks the central axis of the body has never been found in one of Rembrandt’s works.

Although the painter of the »Man with the Golden Helmet« did not have Rembrandt’s skill, it could be shown that he must at least have been in contact with Rembrandt’s workshop. The painter did not use the pigment smalt for colouring details in blue, but for optical reasons and as a bulking agent, as it was in use in the workshop of the late Rembrandt. Rembrandt started to add nearly colourless smalt to all kinds of colours but mainly to dark ones around 1650. Henceforward nearly all backgrounds were mixed with boneblack and smalt, too, as it is done in the background of the »Man with the Golden Helmet«. A large quantity of smalt also is added to the pigment mixture for the brown breastplate.

»Portrait of Hendrickjie Stoffels«

For the »Portrait of Hendrickjie Stoffels« (fig. 5) art historians had suggested that the composition of this painting was influenced by a lost painting by the Venetian artist Palma Vecchio, which was auctioned in Amsterdam during the 1640s by a relative of Rembrandt’s wife Saskia (fig. 6). By a still existing sketch of the lost painting, we know that a similar version by Palma Vecchio is in the Gemäldegalerie Berlin. Her head is resting against her arm, with a relaxed loose-hanging hand. His dispute with Palma Vecchio’s composition, mainly the position of the arm at the doorframe, is revealed...
in the autoradiographs (figs 7-8), and thus the accuracy of the art historian’s suspicion is proven.

Below the arm, that today is supported at the door case there are two positions for a hand, loosely hanging over the armrest of a chair. We can see them because they were blocked out by the background colour. There are no signs that they have been transformed into colour.

A further draft shows her arm angled towards her head. This version was executed in colour, which was then scraped off with a wide spatula, traces of which can be clearly seen in the autoradiograph.

The third autoradiograph demonstrates the addition of smalt. It contributes to form the structure of the red robe and it is added to the colour of the background, which, as can be seen in the last autoradiograph, also contains boneblack. The background thus consists of a mixture of bone black and smalt as it could be demonstrated for the painting »Man with the Golden Helmet«.

The bright folds of the red robe are painted with vermillion. The mercury isotope darkens the film and illustrates a fast and peppy brushstroke with which the paint was applied.

»Jacob wrestling with the angel«, painted in about 1660 (fig. 9)

In the autoradiographs of this painting (figs 10-11) Rembrandt practised to build up a composition that can be particularly well observed. Rembrandt painted first the background, leaving blank the space for the intended foreground blank. The space he left open for the wings is smaller than they were finally painted.

The third and the last film show once again the application of smalt and boneblack in the background.
Part of the success of autoradiography applied to paintings by Rembrandt is that the distribution of the pigment boneblack is so splendidly reproduced. Especially in his later works, Rembrandt made the initial sketch of the composition in boneblack. The last autoradiograph of this painting discloses such a wonderful sketch. With loose and vital brushstrokes, Rembrandt designed the contours of Jacob and the angel. During the sketching process, he corrected the position of the angel’s hand, thus creating the intersecting diagonals of the two bodies which are embraced by the sweep of the angel’s spread wings.

However, probably not all the lines can be attached to a first sketch. Maybe some lines have served to reinforce contours at the end of the genesis of the painting. As autoradiographs show a summation of radiation from all layers, the painting needs to be studied with the stereoscope for a more accurate evaluation. Maybe the position of the reproduced paint...
layer can be located within the paint layers visible at the edges or in open cracks of the painting.

We are happy that this time-consuming evaluation of the autoradiographs is supported by the Andrew W. Mellon Foundation. The foundation funds the set-up of the Rembrandt Database. The plan is a detailed compilation of technical photographs, restoration documentation, archival material and art-historical information on all paintings attributed to Rembrandt. The Gemäldegalerie will make an important contribution because of its extensive collection of works by Rembrandt and the fact that neutron autoradiographs exist from all paintings, which will be published in the database for the first time (www.rebrandtdatabase.org/Rembrandt).

The »Rape of Proserpina«, dated around 1632 (fig. 12)

The intense blue of the sky upsets every Rembrandt connoisseur. Moreover, the sky is painted with lapis lazuli, a blue pigment which, until now has never been found in a painting by Rembrandt, so the prevailing opinion presumes the blue sky to be a later addition.

Nevertheless, the blue lapis lazuli was clearly applied by Rembrandt himself. There is no evidence at all of a later application; furthermore, the researchers had ignored the fact, that lapis lazuli is also present in other parts of the painting with an identical grain (fig. 13). Lapis was used for the sleeve on Diana’s arm below her chin, as well as for the two blue decorations on the quiver (fig. 14). However, the blue sky originally was less intense as we see it today. On the entire surface are the remains of a light reddish-white thin paint application with which the glaring blue was broken into a sfumato.

The structure of the paint layers can very well be observed at the edges (fig. 15). The lapis lazuli on top is under painted with smalt mixed with white lead. Underneath, there is a thick white paint layer, which can be observed along all edges. It covers a rejected composition of which only the paint application at the edges (mainly in grey) can be seen. The
radiological techniques cannot detect this composition because the thick covering paint consists of pure white lead. Therefore, what we see in the X-ray (fig. 16) is not the ground layer but the white layer that hides the first composition. Its application with a firm broad bristle brush can be observed.

In the first autoradiograph (fig. 17), many changes during the genesis of the composition on top of the white hiding layer are already visible. A sketch in brown colour can be seen for several horses in a smaller scale and a block-out for a horse’s head in large scale.

In the dark monotonous vegetation in the right half of the painting, there are leaves that were intensely coloured with copper pigments. Pluto is surrounded by bushes.
In the second autoradiograph (fig. 18), one can observe that the underpainting of the sky with smalt goes far down. In the upper part of the sky, the sodium isotope in lapis lazuli blackens the film. The lower edge seems to be rounded as by circling wiping.

The last autoradiograph (fig. 19) shows the visible composition with the eerie horse turned toward the viewer. The component phosphorus in boneblack darkens the film.

By examining the painting with a stereoscope, no paint application could be found for the head of the horse in large scale. The small-scale version was completed. However, before Rembrandt enlarged the horses into the visible version of today he reduced the deeper colour, but not completely, a red underpainting and some details of the small horses were obtained, which we can find again in the horses visible today.

The decorated neckband of the underlying horse was left, and only slightly enlarged to the left. The red colour of the underlying horse was taken for the cheek piece of the visible head and a yellow pattern was added. In addition, the linkage of the little horse was left, it is blocked out of the light grey colour of the larger horse.

The vegetation behind the little horses was also kept dark, but in more vivid colours, with intensely coloured leaves and flowers. With the enlargement of the horses, they were painted over with brown colour, which today is partially abraded.

The design of the left half of the painting was also more colourful and rich in contrast. Originally, the blue coloured sky went further down. Green leaves behind Pluto jutted into the blue sky.

The contrasting colour was withdrawn for the now visible composition. In the lower area of the sky, the lapis lazuli was wiped away in a circular movement. From the blue, only the light grey underpainting of the sky remained with rests of thicker applied green leaves. The wiped away blue of the sky was replaced by a dark haze. Proserpina’s dress had originally been blue. A thick, deeper blue paint layer can be observed. The autoradiograph shows the darkening by the blue copper pigment. On the left hand side, the dress fell almost vertically downwards.
The findings of the autoradiographs indicate that the creation of the painting must be scheduled for a longer period of time. The style of the colourful version with horses in small scale suggests an origin before 1630. The withdrawal of contrasts and an observed separation of paint layers suggest that the increase in the scale of the horses and the transformation in monotone colours only happened within a longer time interval. The size of the figures of the version with the little horses was not changed. The figures together with the initially small horses resulted in a composition that was harmonious in itself, with a strong stress on the diagonal of the painting (fig. 20).

The enlargement of the horses increases the drama tremendously, the viewer recoils from the horse, which gives off an impression as though it were jumping out of the picture. Proserpina’s dress was amended in such a way that the speed of what happens and the desperate pulling on the garb by the playmates can be felt with immediacy. By the monotonous dark colouring of the right background, the abduction of Proserpina from the light-flooded world into the darkness of the shadow world is emphasized as the topic of this composition.

«Minerva», dated around 1631 (fig. 21)

The genesis of this painting is even more complicated than in the «Rape of Proserpina». Probably three different versions were tried before the visible composition. As the examination with the stereoscope proved, in the first version, a figure stood at the right hand side of the painting. The figure was then moved towards the centre of the painting. A blocked out area above the centre of the painting might be the head of a sitting figure, but seems to be too large (fig. 22).
Up to 16 overlaying paint layers could be observed. Two of them served to reject the according former version.

The first covering layer is rather thick and mixed with white lead bound in a medium containing protein. The second covering layer consists of pure white lead and is applied in different thickness, but mostly razor-thin. This layer marks the beginning of the now visible version, which also includes several changes.

The first thick covering layer becomes apparent in the X-ray (fig. 23) and shows that in the lower left part it was removed again. In the still life with books all layers of paint were removed. The paint layer is located directly on the wood and stayed rather flat during the aging process.

The X-ray also shows pentimenti in Minerva's dress and coat. The highlight of folds not corresponding with the visible composition can be seen.

In the infrared reflectograph (fig. 24), a hanging down tapering fold of a tablecloth can be observed. Its shape conforms with the lower part of the removed part visible in the X-ray.

The shape of the fold of the tablecloth in turn seems to be nearly identical to the fold in the painting »Minerva« in the Mauritshuis, ascribed to the circle of Rembrandt and dated a bit earlier than our painting. It still needs to be clarified in which context the two paintings could be.
The pronouncement by many Rembrandt researchers that Rembrandt did not use lapis lazuli is again disproved. In this painting, too, lapis lazuli was used for the ornaments in Minerva’s dress (fig. 25).

A comparison of neutron autoradiography with scanning macro-XRF

The method to scan a painting by XRF has been in use for some years. Along the way, the method has been constantly improved and still is. The device is now portable and can capture an area of $80 \times 60 \text{ cm}^2$. Only recently, images of XRF scans were presented of several paintings by Rembrandt from the Rijksmuseum in Amsterdam in good quality and with interesting findings. Since with this method different coloured underlying paint layers can be made visible, it is now discussed as an alternative to autoradiography.

To determine the advantages and disadvantages of both methods in a direct comparison, four already autoradiographed paintings were scanned by XRF in the Gemäldegalerie Berlin in November last year. The scans were produced by Matthias Alfeld from the University of Antwerp, who is writing his doctoral thesis on scanning macro-XRF with his self-constructed scanner.

One of the scanned paintings »Adoration of the shepherds«, attributed to Pieter Cornelisz Rijck (fig. 26) had been used as a test panel for the activation at a neutron guide. It contains the colour palette common in the 17th century, but is of no art historical interest. Nevertheless, the findings are quite interesting. The painting is on canvas, which has been adhered to a wooden panel. The autoradiographs disclosed deeper lying paint applications that proofed that the canvas for the small painting had been cut out from a large-format painting.

In the X-ray (fig. 27) one can see the distribution of white lead and some absorption by mercury in vermilion and copper, here in the blue pigment Azurite. The texture of the canvas is clear to see and a rectangle of the large format painting is visible.

Comparison to the XRF scan showing the distribution of lead (fig. 28) shows that though the resolution of the scan could be improved by a smaller step size, it will never achieve the sharpness of a film. The rectangular and the structure of the canvas are not visible. The fluorescent radiation is detected only from layers near the surface. This may be of advantage in cases where the readability of an X-ray is prevented by a strong absorption of the carrier of the painting.

The first autoradiograph (fig. 29) is to show the distribution of manganese in brown colours. Brown earth pigments also contain iron, which does not show in autoradiography.
Examining the first autoradiograph, a presumed disadvantage of autoradiography becomes obvious. The individual isotopes cannot be shown separately on the films. However, it is possible to determine the isotope by comparing all autoradiographs regarding the increasing or decreasing darkening. In addition, the individual colour areas are gamma spectroscopically determined.

The sharp drawing of the film is impressive. The long stroke of the brush in the roof, the short one applied for the grass and a pattern in the gown of the figure at the right edge of the painting can be seen. Even the cracks in the paint layer are visible. A deeper brown paint layer running in a vertical bow appears in the same sharpness.

The XRF scans showing the distribution of Mn (fig. 30) and Fe (fig. 31) illustrate the advantage that each element can be shown separately, though again the resolution of the scan compared to the autoradiograph is much worse.

The second autoradiograph (fig. 32) serves mainly to show the distribution of copper pigments.
Mn-isotope has decayed; the darkening of arsenic in the sky has increased. The darkening of copper is most intense. From the cut out painting underneath, a paint layer running vertically on the right hand side can be seen. In the middle, an ornament is visible. The XRF scan shows the exclusive distribution of copper (fig. 33), the appearance of the deeper vertically running paint layer and the ornament is weakened considerably; the fluorescent radiation is absorbed by covering paint layers.

The XRF scan showing the distribution of arsenic (fig. 34) documents the presence of smalt in the sky. The existence of smalt can also be proven by the distribution of Ni (fig. 35).

In the fourth autoradiograph (fig. 36), copper in the landscape and the tree has decayed. It shows the darkening by the mercury isotope in vermilion. It is added to the flesh tone of the figures and to the garment of Joseph in the middle. The upper part of the shepherd at the left edge and the trousers of the
one on the right hand side seem to be painted with pure vermillion. The sky is painted with smalt, its components arsenic and cobalt darken the film. A structure of the large format painting of which the canvas for this painting was cut out becomes clearly visible. A vertical bow in a deep paint layer is painted with boneblack. The darkening by the phosphorous isotope reproduces the long drawn brushstroke – as well as the wet-in-wet technique with which the ornament we have seen in the second autoradiograph was applied. As phosphorus cannot be analysed with XRF, Calcium (fig. 37) serves as proof for the presence of boneblack. However, the reflected X-radiation is
quickly absorbed by covering paint layers. Only when the calcium containing layers, like the ground or boneblack, are near the surface, they can be detected. In this case, the deep paint layer of boneblack is impossible to prove, just as would be a first sketch in boneblack in a painting by Rembrandt. XRF, however, can demonstrate the distribution of other elements, which remain invisible in autoradiography. The distribution of the pigment lead-tin-yellow cannot be seen in autoradiography, except when it is on the surface of the painting and thus in close contact to the film. Iron also cannot be detected by autoradiography. Here, XRF definitely has an advantage. In the painting »Portrait of Rembrandt« by Govaert Flinck (fig. 38), a large pendant of the necklace is invisible in all autoradiographs but shows up clearly in the XRF scan (fig. 39).

The result of comparing both methods is that scanning macro-XRF cannot replace autoradiography. The sharp reproduction of the brushstroke even in very deep paint layers is unbeatable. The key pigment for the late Rembrandt, boneblack, can only be proven by autoradiography.

In contrast to autoradiography in XRF more elements can be analysed. The distributions of single elements are visualised in separate images. XRF seems to be suited best for paintings with thin layers of paint as the X-ray fluorescence is very easily absorbed by overlying layers of paint. However, this feature may also be helpful for the interpretation of X-ray or autoradiography. Therefore, both methods actually complement each other. Both together would increase the possibilities for the analysis of deeper paint layers.

The valuable and irreplaceable paintings are very sensitive to vibrations and climatic changes. Here XRF has a distinct advantage. The examination with XRF takes place in the rooms of the museum. The painting does not even have to be removed from its place. For autoradiography, however, the painting has to be transported to the reactor and is subjected to several handling during the examination. And the investigation is connected with radioactivity, a scary word for art historians and conservators, although the activation always decays to safe levels, even zero, in reasonable waiting times.

Notes

1) The longer wavelengths of infrared radiation penetrate thinly applied layers of paint. Underdrawings on a white, reflective ground and changes in the paint layers can be made visible.
2) X-rays penetrate through paint layers but are absorbed by higher-density materials like pigments containing lead or mercury. In an X-ray, these pigments show up lighter or even white depending on the thickness of application.
3) See detailed description in Alfeld et al. 2015.

General references

The Examination of Paintings by Rembrandt with Neutron Autoradiography and a Comparison of Neutron Autoradiography with Scanning Macro-XRF

For over 30 years, neutron autoradiography is in use for the examination of paintings from the Gemäldegalerie, Staatliche Museen zu Berlin, in cooperation with the Helmholtz-Zentrum Berlin. It expands the spectrum of colours by a multiple whose distribution in deeper layers of paint can be made visible. Together with the X-ray photograph and infrared reflectography a comprehensive insight into the genesis of a painting is made possible. By additional application of gamma spectroscopy the darkenings on the autoradiograph can be assigned to special isotopes. The use of film allows a particularly good reproduction of the brush stroke, the technique of paint application and the conservation status (condition) of the painting. Autoradiography therefore provides art historians and conservators with a wide scope of possible interpretations. By now about 70 paintings have been examined, mainly those by Rembrandt and his circle, but also works by Vermeer, Titian, Jan Steen, Frans Hals, Rubens. The results obtained by scanning macro-XRF and neutron autoradiography on the same paintings are compared.

Keywords

neutron autoradiography / autoradiography / paintings / Rembrandt / MAX RF / micro-XRF mapping / macro-XRF / μ-XRF / X-ray fluorescence elemental scanning / X-ray fluorescence elemental imaging / scanning macro-XRF