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Spatially resolved synchrotron radiation induced X-ray fluorescence analyses of rare Rembrandt silverpoint drawings

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ABSTRACT New analyses of a series of very rare silverpoint drawings that were executed by Rembrandt Harmensz. van Rijn (1606–1669) which are kept today in the Kupferstichkabinett (Museum of Prints and Drawings) of the State Museums of Berlin are reported here. Analysis of these drawings requires particular attention because the study has to be fully non-destructive and extremely sensitive. The metal alloy on the paper does not exceed some hundreds of $\mu g/cm^2$. Therefore, synchrotron radiation induced X-ray fluorescence (SR-XRF) is – together with external micro-proton-induced X-ray emission – the only well-suited method for the analyses of metalpoint drawings. In some primary work, about 25 German and Flemish metalpoint drawings were investigated using spatially resolved SR-XRF analysis at the BAMline at BESSY. This study enlarges the existing French–German database of metalpoint drawings dating from the 15th and 16th centuries, as these Rembrandt drawings originate from the 17th century where this graphical technique was even rarer and already obsolete. It also illustrates how SR-XRF analysis can reinforce art historical assumptions on the dating of drawings and their connection.

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1 Introduction

Nowadays, artists have a large panoply of drawing materials at their disposal. But when looking for drawing materials used by artists in Europe in earlier times only little information is available. Hardly any ancient drawing instrument is conserved. Therefore, the only possibility to get representative insights into former drawing techniques is the analysis of the drawings themselves.

Metalpoint drawings generally belong to the most precious and rarest treasures of graphical art collections; thus, any chemical analysis applied has to be fully non-destructive. The drawings were essentially created during the Renaissance (1400–1600) and are characterised by extremely thin grey-brownish marks on paper which was necessarily coated before use. Art history generally allows the attribution of a drawing to a certain artist or school, even if some drawings are not signed. If their authenticity cannot be identified unambiguously, in some special cases further information can be gained from physico-chemical analyses.

The aim of this study is to obtain a better knowledge of artists' materials, to study alteration phenomena and to define new comparison criteria based on a chemical fingerprint contained in the metal marks. So far, results on about one hundred silverpoint drawings on coated paper by Italian, Flemish and German artists have been obtained with external beam micro-proton-induced X-ray emission (micro-PIXE) at the C2RMF in Paris and with spatially resolved synchrotron radiation induced X-ray fluorescence analyses (SR-XRF) at the BAMline/BESSY in Berlin [1–3].

In this work, a series of three outstanding drawings by Rembrandt Harmensz. van Rijn (1606–1669) on coated parchment were investigated: 'the portrait of his wife Saskia' (KdZ1152, Berlin) dated to 1633 thanks to the presence of an inscription made by the master himself (Fig. 1) and two landscape sketches on the recto and verso of one sheet (KdZ 2317r/v, Berlin) (Fig. 2a, b) [4–6]. They are kept today in

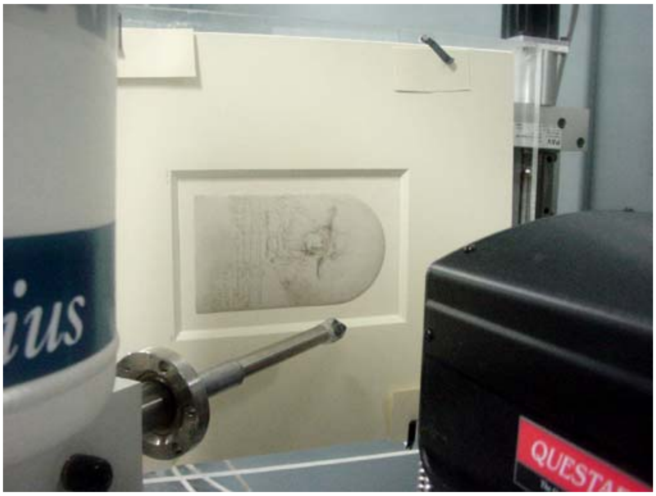
FIGURE 1 Drawing by Rembrandt Harmensz. van Rijn, Portrait of Rembrandt's wife Saskia with inscription 1633, State Museums of Berlin, Kupferstichkabinett (KdZ 1152). Size: 19.6 × 11.8 cm, mounted in front of the BAMline with Si(Li) detector and long-distance microscope

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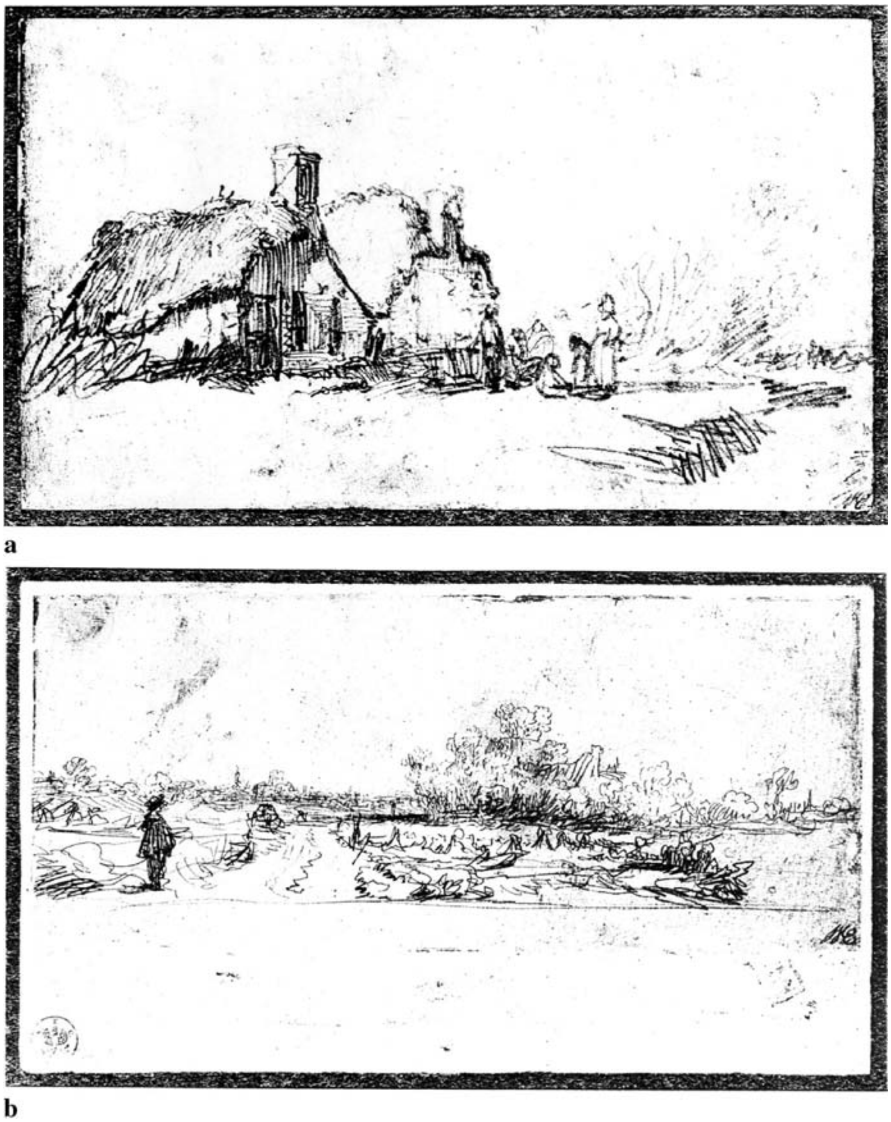

FIGURE 2 Rembrandt Harmensz. van Rijn, Landscapes, State Museums of Berlin, Kupferstichkabinett (KdZ 2317r/v), (**a**) recto, (**b**) verso. Size: 10 × 18 cm

the Kupferstichkabinett (Museum of Prints and Drawings) of the State Museums of Berlin. The study especially focuses on the comparison of the chemical composition of the metalpoint(s) used for the portrait of Saskia and its inscription, as well as the one(s) used for the two landscapes. Indeed, the dated inscription allows an unambiguous attribution and dating of the Saskia drawing, if the figure and the inscription – the handwriting is typical for Rembrandt – were created with the same metalpoint. On the contrary, the two landscape sketches can only be dated stylistically. Therefore, a comparison of the chemical composition of the metalpoint(s) used for the portrait of Saskia and the two landscape drawings might give further art historical information.

In addition, only three sheets with five Rembrandt metalpoint drawings exist today (two sheets in the Berlin Kupferstichkabinett investigated here and a third in the Boijmans van Beuningen Museum of Rotterdam, also drawn on both sides [5, 7]). Thus, it is expected that the chemical analysis might provide new insights into why Rembrandt used this rare and already obsolete technique at his time.

2 Experimental

Prior to the SR-XRF analysis, the drawings were examined by optical microscopy at the Kupferstichkabinett to distinguish different drawing materials and, hence, to decide on representative analysis points of different parts of the drawings. The observations were made with a magnification of 25 using a Leica microscope equipped with a camera.

An ultra-sensitive and non-destructive method is needed for elemental analysis of metalpoint drawings because very thin scattered layers of metal particles are deposited on the drawing support. In this case, the support consists of parchment coated with a layer of bone white, a calcium phosphate obtained from burnt bone. Former analysis showed that SR-XRF provides the sensitivity required to quantify the chemical composition of the metalpoint. This is due to linear polarisation that results in a lower scattering background, and a higher photon flux compared to conventional XRF with X-ray tubes [2]. The spatial resolution is necessary in order to obtain a high metal to paper background ratio for the analysis of the metal marks.

Tests on historical parchment samples have ensured that the used SR-XRF measurement conditions allow a completely non-destructive analysis of the drawings on parchment. Although PIXE [1] seems to be a better-suited method at first glance, extracting signals from the very surface region of a drawing, PIXE has to be carried out at very low beam currents due to the risk of local damage of the sheets. In the case of SR-XRF, this risk is negligible allowing higher fluxes thanks to a sophisticated selection of measurement conditions. The main damage risk is more likely linked with climatic changes such as temperature and humidity during analysis and transportation than X-ray radiation.

A spatially resolved SR-XRF set-up is mounted for analyses at the hard X-ray beam line (BAMline) [8] at the synchrotron BESSY. A superconducting wavelength shifter with a maximum field of 7 T is used as X-ray source. A W/Si double-multilayer monochromator (DMM) produces a monochromatic X-ray beam with an energy of 33 keV. The beam is focused to a beam size of $100 \times 200\,\mu\mathrm{m}^2$. The drawings are mounted in air in a special frame for passe-partouts on a motorised *xyz* stage at an angle of 45° to the X-ray beam. Fluorescence signals are collected for 300 s each by a Si(Li) detector covered with a polyethylene filter at 90° with respect to the incident beam. The polyethylene filter protects the detector against visible light. A video system and a long-distance microscope permit us to observe and to select the analytical points on the drawings.

Data processing is performed by means of AXIL [9]. Relative concentrations of minor components of the silver marks are determined using a procedure based on different silver standards applied on recent paper. So, it is ensured that the silver layer thickness of the standards is of the same order of magnitude as that of the original drawings.

The chemical analysis of silverpoint drawings – even by very sensitive techniques – is restricted to the detection of some minor elements (detection limit of about 0.5 wt. %) of the silver marks because of several intrinsic factors linked with the constitution of these drawings. The same reasons also explain the relatively high and variable uncertainties of the concentration values obtained for minor elements: when using high-energy X-rays for chemical analysis, incident and fluorescence X-rays pass completely through the drawing. Thus, the silver mark cannot be analysed separately from the backing. Marks on the back can also contribute to the detected spectrum of the front. Their simultaneous analysis cannot always be avoided. The silver amount deposited on the paper is very low (areal density in the order of $50\,\mu\mathrm{g/cm}^2$). They represent small scattered particles and no continuous lines. In addition, the backing is quite heterogeneous on the microscopic scale. All these factors made it necessary to establish a quantification procedure involving different normalisation procedures. Normalisation to an internal element (Sr, mainly from the coating), whose concentration is assumed to be homogeneous, is necessary prior to background subtraction to account for the contribution of X-ray fluorescence of elements from the parchment and the coating. The spectra of the marks and of the backing show a significant difference of the two intensities of the Ag K_α lines. By contrast, the analogous differences of Cu K_α and Zn K_α are much smaller. This fact, together with the microscopic heterogeneity of the preparation layer and the support itself, explains the relatively high uncertainties of the concentration values of these elements. After the subtraction of the background signal, normalisation to Ag counts is performed because the excitation spot size is significantly larger than the silver deposit on parchment. Finally, we used a thin-layer approximation without self-absorption correction to calculate concentrations. Indeed, the measured intensity for one element becomes independent of the concentrations of the other elements for thin samples [10]. This procedure enables the determination of the characteristic chemical fingerprints of the metal stylus or styli used for the inscription, the figure and the landscape sketches, respectively. Five to ten measurements on one item are performed and averaged to obtain the chemical composition of silver marks on a drawing.

3 Results and discussion

3.1 *Observation by optical microscopy*

3.1.1 Saskia drawing. This portrait shows a very homogeneous, well-prepared and thick white coating in a very good state of preservation. It is only scraped and renewed at a small area next to the hat of ‘Saskia’. The portrait is executed with metalpoint marks of different widths. Only two small free zigzag lines, probably made of black chalk, are observed in the garb and next to her hand (Fig. 3a). In her face, some fine scratches originating from the metal stylus are visible (Fig. 3b).

FIGURE 3 Optical micro-photograph (×25) of (**a**) metalpoint zigzag and black chalk marks and (**b**) scraped metalpoint marks on the figure of ‘Saskia’

The inscription is also written with a metalpoint. Next to the letter ‘ÿ’, there is also a mark of another material. It could probably be black chalk.

3.1.2 Landscape sketches. These drawings also show a very homogeneous graphical technique. The parchment coating is coarser and brush strokes are clearly visible. Generally, the drawing on the back (verso) consists of fine and large marks similar to those observed on the ‘Saskia’. This is not the case on the front (recto). Here, we find relatively large marks.

3.2 *SR-XRF analyses*

The silver marks of the figure and the inscription of the ‘Saskia’ drawing as well as those of the landscape sketches have been successfully analysed (Fig. 4). Detailed analytical results are given in Table 1. All parts of the drawings are realised with metalpoint, except some small marks like the zigzag mark in the garb, the mark next to her hand or the one in the inscription. These marks are executed with another drawing material than silverpoint as already assumed from optical microscopy observation and confirmed by the SR-XRF spectra (Fig. 4). It is probably black chalk because the material contains more iron and zinc than the backing and no silver. Some lead could also be detected in different parts of the drawings which might be either traces of leadpoint marks or more likely of lead white in the preparation layer.

The metal marks of the ‘Saskia’ figure are a copper- and mercury-containing silver alloy. The copper concentration is (11.6 ± 2.8) wt. %. Traces of zinc (< 1 wt. %) are also identified. The chemical composition of the inscription on the ‘Saskia’ is also a copper- ((11.2 ± 2.8) wt. %) and mercury-containing silver alloy with traces of zinc. The recto landscape sketch is drawn with a silverpoint containing (13.1 ± 5.4) wt. % copper and traces of zinc. Mercury is also present in variable concentrations in the marks. The marks of the verso drawing of the landscape showed a silver alloy with (11.8 ± 2.3) wt. % copper, some mercury and zinc traces. The slightly higher copper content of the recto landscape drawing compared to ‘Saskia’ and the verso landscape drawing can be due to a more heterogeneous preparation layer or to the analysis of silver marks of the recto and the verso simultaneously. Therefore, we cannot distinguish between different silver alloys in these cases within measurement uncertainties. Comparable copper concentrations in the silver marks of the figure of ‘Saskia’, the inscription and the landscape sketches indicate

Analysis point and description	Cu content in the silver marks/ wt. %	Zn in the silver marks/ 0.5 wt. % $< x <$ 1 wt. %	Hg in the silver marks	Pb in the drawing (lead white or traces of a leadpoint line)
Saskia (KdZ 1152, Berlin)				
Portrait. Foulard under hat	10.4	*x*	*p*	–
Portrait	8.8	*x*	*p*	–
Large zigzag line. Garb	16.7	*x*	*p*	*p*
Portrait	14.6	*x*	*p*	*p*
Portrait	10.0	*x*	*p*	*p*
Separation line	7.7	*x*	*p*	–
Inscription. 1. Line	14.6	*x*	*p*	*p*
Inscription. 2. Line	11.7	*x*	*p*	*p*
Inscription. 3. Line	8.0	*x*	*p*	*p*
Inscription. 4. Line	10.5	*x*	*p*	*p*
Separation line	11.3	*x*	*p*	*p*
Hatching	12.4	*x*	*p*	*p*
Hatching	11.8	*x*	*p*	*p*
Mean value	11.4 ± 2.7			
Landscape recto (KdZ 2317, Berlin)				
Hatching. Right house	26.3	–	*p*	–
Sod	10.7	*x*	*p*	*p*
Upper sod	19.1	–	*p*	–
Feet of the woman	11.2	*x*	*p*	–
Abdomen of the man	12.8	–	*p*	–
Right house gable	13.2	–	*p*	–
Grass next to the left house	11.3	–	*p*	–
Mean value	13.1 ± 5.4			
Landscape verso (KdZ 2317, Berlin)				
Haystack	10.1	*x*	*p*	–
Haystack	11.9	*x*	*p*	–
Hat	8.8	*x*	*p*	–
Landscape left	16.8	*x*	*p*	*p*
Grass. Left	10.1	*x*	*p*	*p*
Grass. Left	13.0	*x*	*p*	*p*
Town. Tower	11.9	*x*	*p*	–
Landscape	12.2	*x*	*p*	*p*
Trees	11.2	*x*	*p*	*p*
Mean value	11.8 ± 2.3			

TABLE 1 Detailed SR-XRF data of measurement points on the silver marks of the drawings. *p* = present, – = under the detection limit

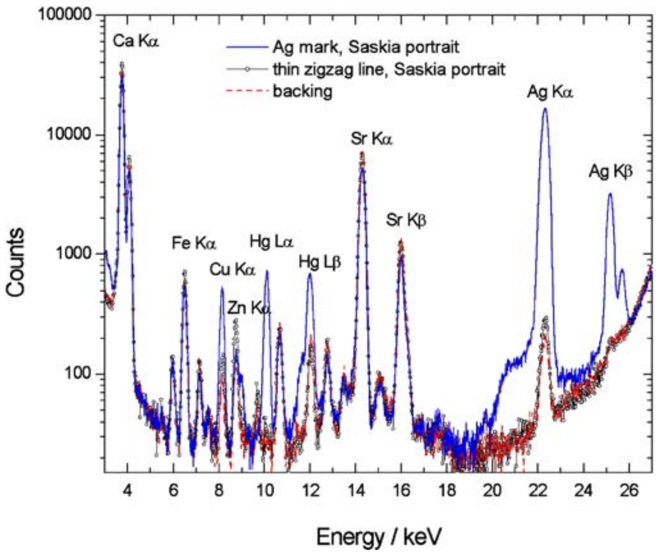

FIGURE 4 33 keV SR-XRF spectra of marks on the portrait of 'Saskia', black chalk zigzag marks and backing

that it is highly probable that all parts were executed with the same type of silver stylus.

This result does not exclude the hypothesis that all drawings might have been created within a very short time period, perhaps in 1633. Stylistically, the drawings of the landscapes could also be realised some years later, between 1633 and 1636. It is indeed possible that Rembrandt used the same silverpoint in a time period of three years as he probably did not possess several ones. Other artists such as Albrecht Dürer are also known to have executed a series of drawings within a relatively short period of time with one metalpoint. This was evidenced during a former study of 15 drawings originating from a sketchbook of his travel in the Netherlands in 1520–1521 [2].

The presence of mercury is more likely due to an alteration process than reflecting the original composition of the silver stylus used by Rembrandt. This assumption is supported by several facts: (1) mercury has a high chemical affinity to silver and is easily taken up from the atmosphere as laboratory tests showed, (2) one of the only conserved silver styli dating from the 16th century on the so-called 'Karlsruher Skizzenbuch' contained trace amounts of mercury and not concentrations in the order of several tens of wt. % as found in the silver marks of the drawings [11] and (3) a silver stylus containing high amounts of mercury is too hard to be used for fine hand drawings even on coated parchment.

4 Conclusion and outlook

This work showed that spatially resolved SR-XRF is a powerful tool for the non-destructive study of precious metalpoint drawings. The study of three outstanding drawings by Rembrandt supplemented previous results on German, Flemish and Italian metalpoint drawings [1–3]. These investigations evidenced that the characteristics of the silverpoint used for drawings by Rembrandt in the period of 1633 until 1636 are very similar to those observed on metalpoint drawings of the 15th and 16th centuries. The question why Rembrandt used this already obsolete graphical technique could unfortunately not be solved by chemical analysis. However, the results are highlighting in a more general manner the performance of extremely sensitive non-destructive analyses applied to fragile drawings and evidence that their use could represent a beginning for new perspectives in art historical interpretation.

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