

NON-DESTRUCTIVE INVESTIGATIONS OF DÜRER'S SILVER POINT DRAWINGS BY PIXE AND SR-XRF

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The use of silver points is one of the most delicate and precious drawing technique used by Renaissance's artists in Europe. Little information is available on the chemical composition of these drawings because analysis needs to fulfil two conditions: it has to be fully non-destructive and extremely sensitive. Indeed, the metal alloy on the paper does not exceed some hundreds of $\mu\text{g}/\text{cm}^2$. We report the analysis of some sheets of the sketchbook that Albrecht Dürer drew during his journey through the Netherlands in 1520/1521. Six drawings, conserved in the musée Condé of Chantilly (France) were investigated by Proton Induced X-ray Emission (PIXE). Seven other drawings of the same sketchbook are conserved in the Kupferstichkabinett Berlin (Germany). Spatially resolved synchrotron radiation induced X-ray fluorescence (SR-XRF) was used to analyse six of these drawings. The results obtained on Dürer's drawings in the sketchbook indicate a characteristic composition of 87-96% silver, 3-12% copper and traces of zinc. In addition, a high amount of mercury was detected in the silver strokes, which we attribute to a contamination from atmosphere.

Introduction

On July 15th 1520, Albrecht Dürer left his living place Nürnberg to go on a trip to the Netherlands. The goal of this trip was to assure the artist's pension he received from the Emperor Maximilian who had died recently before. During seven months, he wrote a diary, which allows us to follow him during this travel [1]. Besides, in a sketchbook now divided, he drew sketches, portraits and landscapes.



Fig. 1.A. Dürer, *A young and an old woman of Bergen-op-Zoom*, Chantilly, inv. 891v^o.



Fig. 2.A. Dürer, *Sitting bishop and portrait of a man with a fur cap*, Berlin, KdZ 34r^o.

The musée Condé of Chantilly (France) and the Kupferstichkabinett of Berlin (Germany) conserve several sheets (13 x 19 cm) of this sketchbook. They are drawn on both sides with metal point on a white preparation layer (fig.1, 2). The large number of drawings, made with a rare and precious technique by only one artist in a short and well-informed period, represents an exceptional opportunity to get new insights in this graphical technique.

Analytical methods

As drawings are precious and fragile, sampling is not appropriate and the analysis must be fully non-destructive. A high sensitivity is also required because very thin layers of materials are applied on the paper or the parchment. Indeed, the sample mass corresponding to the deposited metal alloy does not exceed some hundreds of $\mu\text{g}/\text{cm}^2$. For these reasons, proton induced X-ray emission (PIXE) with an external beam has been used for some years in Paris to analyse metal point drawings [2, 3]. As such an external proton beam was not available to analyse the drawings from Berlin, spatially resolved synchrotron radiation induced X-ray fluorescence (SR-XRF) was tested. Prior to the analysis of ancient drawings, reproduced silver strokes were prepared in order to check the non-destructiveness of this technique, to adjust the parameters of beam line and to determine a quantification routine. SR-XRF was revealed to be fully non-destructive and to provide the sensitivity required for the quantitative determination of the chemical composition of the silver point.

SR-XRF experimental set-up

We used the hard X-ray synchrotron beamline (*BAMline*) at BESSY II operated by the Bundesanstalt für Materialforschung und -prüfung [4] to determine major and minor element contents in the silver point strokes of the drawings. At the *BAMline* set-up a super conducting wavelength shifter (WLS) with a maximum field of 7 Tesla is used as an X-ray source. The experimental conditions are listed in table 1 and described more in detail elsewhere [5].

Data evaluation and determination of yielded characteristic photons were performed by means of AXIL (fig. 3). Spectra were normalised to the Fe K_{α} peak counts and an average value over three measurements of the white ground and of the stroke, respectively, was calculated. The mean value of the ground was subtracted from that of the strokes in the corresponding drawing. Cu and Ag concentrations were determined using three standards corresponding to reproduced silver strokes on normal paper whose element concentration had been determined on the used silver point with atomic absorption spectroscopy (AAS) and on the reproduced stroke using PIXE. In the case where Zn counts significantly surpass the amount of the backing, a Zn containing solution deposited on filter paper was used as standard.

PIXE experimental set-up

An external PIXE beam line was developed on a 6SDH-2 2MV tandem NEC Pelletron accelerator in the C2RMF to provide *in situ* and non-destructive analysis of museum objects [6]. The experimental set-up for the presented measurements is listed in table 1. Quantitative analysis requires the knowledge of the X-ray yield of each element. These are obtained with thin standards of compounds or pure elements whose

concentration in $\mu\text{g}/\text{cm}^2$ are known. After analysis of drawing strokes (fig. 4), self-absorption correction is calculated and white ground contribution is subtracted. This method needs a precise beam monitoring, *i.e.* a constant number of protons for each analysis; this is achieved by measuring the Si K_{α} signal emitted by the exit window [7].

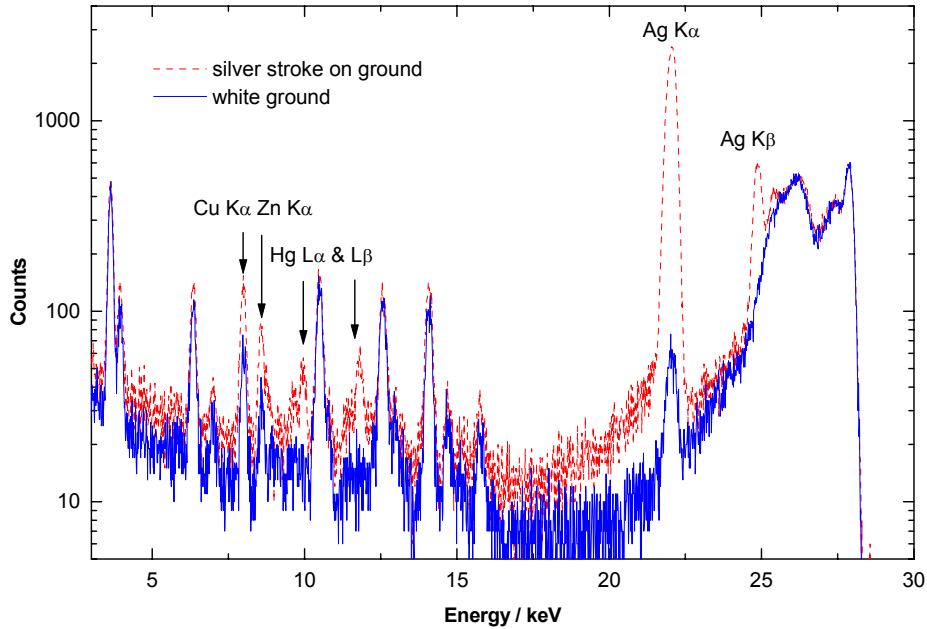


Fig. 3. SR-XRF-spectra (28 keV excitation energy) of a silver point stroke and of the preparation layer of “*Sitting bishop and portrait of a man with a fur cap*” (Kupferstichkabinett Staatliche Museen zu Berlin, KdZ 34r°).

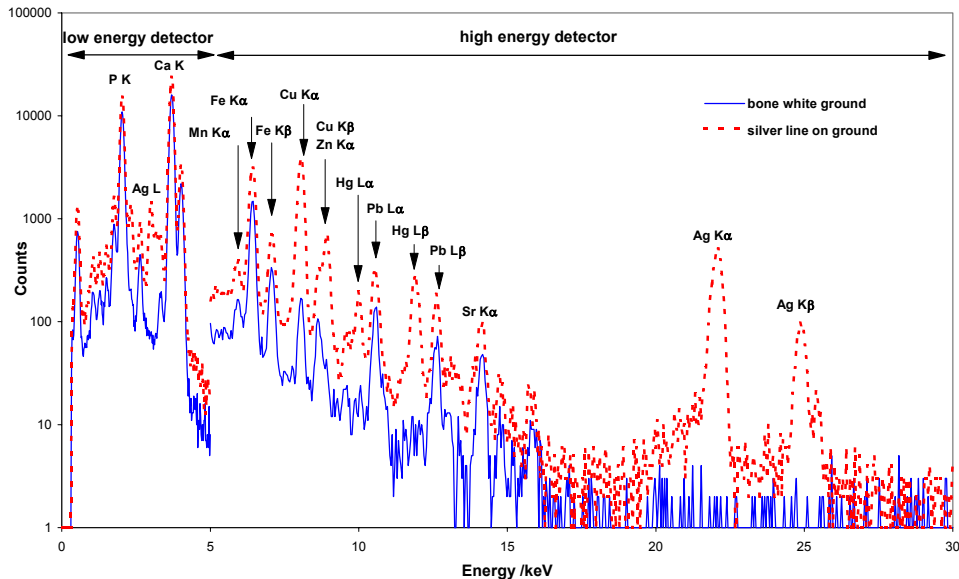


Fig. 4. 3 MeV PIXE spectra of a silver point stroke and of the preparation layer drawing on “*A young and an old woman of Bergen-op-Zoom*” (Chantilly, musée Condé, inv. 891r°).

Comparison of SR-XRF and PIXE

The main characteristics of both techniques are summarised in table 1. An important feature is the different penetration depth of the primary beams. PIXE provides a surface analysis and seems to be more suitable for drawing analysis than SR-XRF. However, the low sensitivity of SR-XRF for surface materials is compensated by the high beam intensity and the transmission of X-rays through the drawing avoids particles deposition in the sample, as it is the case for PIXE.

Table 1. Main characteristics and parameters of SR-XRF and PIXE set-ups.

Method	SR-XRF	PIXE
characteristics	non-destructive, even with white radiation	non-destructive with a low beam current (<500pA)
spatial resolution-beam size	400 x 100 μm^2	100 μm diameter
depth of analysis	excitation and fluorescence X-rays completely pass through the sheets	< 100 μm (proton range) but depends on energy of X-rays
energy and nature of incident beam	28 / 30 keV X-rays	3 MeV protons
atmosphere between sample and detector	air	He
measurement time	300 s	300 s
detector type and filters	Si(Li) 10 mm ² , super ultra thin AP1.4 window, 30 μm Al filter	Si(Li) 10mm ² , Si ₃ N ₄ window; Si(Li) 50mm ² Be window, 50 μm Al filter
detectable energy range	3-30 keV (K to Ag via K line)	1-35 keV (Na to U)

The quality of SR-XRF and PIXE analyses is affected by some intrinsic features linked to the constitution of the drawings:

- The primary beam spot can partially cover the silver stroke on the drawing.
- The thickness of the stroke is always smaller than the penetration depth of the primary beam, even in the case of protons.
- Drawing strokes are not continuous lines: microscopic observation revealed spotted strokes with the paper support visible between the scattered metal particles.
- In SR-XRF spectra of the ground preparation, an Ag K α peak can be visible. This results from the analysis of Ag traces of the backside of the drawing.

In consequence, elements of the preparation layer are always detected when analysing a silver stroke. Thus, the subtraction of the contribution of the preparation layer cannot be accurate. In the case of SR-XRF, normalisation of the spectra to the Fe K α counts, an element present in the paper, is performed prior to the subtraction of the preparation layer contribution from that of the silver stroke in order to limit the error introduced by the non-continuous character of the silver stroke and the simultaneous analysis of the ground.

Comparison of analyses of reproduced silver stroke on paper by SR-XRF and PIXE

with bulk analyses of the silver points by AAS

Three different silver points were applied on normal paper and analysed by SR-XRF and PIXE using the same experimental conditions as described above. The silver pens (20 mg) were then diluted in 20 ml HNO₃ (6.5%) and analysed by means of AAS (PU 9100, Philips). The obtained results on Ag, Cu and Zn are listed in table 2. Other elements (Sn, Pb, Au and Cd) were present in trace amounts.

The comparison of the obtained concentration values shows a good agreement of experimental results determined by each technique. That means that the results obtained by the chosen PIXE and SR-XRF set-up are mutually comparable. Furthermore, these results indicate that the analysed composition of the silver stroke represents the bulk chemical composition of the silver point used. It enables us to conclude on the initial chemical composition of the used point by the artist when analysing ancient metal point drawings.

Table 2. Composition of silver points determined by AAS, SR-XRF and PIXE. The sum of Ag, Cu and Zn corresponds to 100 wt.%.

Material Method	Ag (wt.%)			Cu (wt.%)			Zn (wt.%)		
	AAS	SR-XRF	PIXE	AAS	SR-XRF	PIXE	AAS	SR-XRF	PIXE
Silver point fixed on Meder book (1909)	98.470	96.4	98.5	1.510	2.7	1.5	<0.001	0.9	n. d.
Silver pen 1	92.660	91.6	91.8	6.680	7.6	8.2	0.002	0.8	n. d.
Silver pen 2	93.300	92.8	92.7	7.300	7.1	7.0	0.007	0.1	0.3

Analyses of Dürer's drawings

The preparation layers

All the Dürer's drawings from Chantilly [8] and Berlin were created on paper sheets covered with a white preparation layer. PIXE analysis showed the presence of calcium and phosphorus whereas SR-XRF analysis only revealed the presence of calcium (phosphorus cannot be detected by this experimental set-up). Nevertheless, all ground layers are probably made of bone white as the sheets come from one sketchbook and Cennino Cennini already indicated this preparation procedure in his book on artist's techniques [9]. In addition to bone white, a small content of lead white was detected in all preparation layers.

The silver point strokes

The analytical results obtained on the drawings from the sketchbook, which were analysed in Paris and in Berlin, are listed in the table 3. The results show a similar composition of the silver point(s) used for the realisation of the drawings in Dürer's sketchbook corresponding to a silver alloy containing between 4 and 12 wt.% of Cu, except in the partial drawing of the "man with a fur cap" (Berlin KdZ 34r^o) having the chemical composition of 13.0 wt.% of Cu, 5.3 wt.% of Zn and 81.7 wt.% of Ag. This indicates that all drawings except one in the sketchbook were realised with the same point or at least with silver points having the same chemical composition. This conclusion is consistent with art historical sources that one stylus was fixed to the

sketchbook and used for the drawing [10].

Table 3. Composition of the silver point of the Dürer's drawings. The date of each drawing was inferred from the travel diary written by Dürer [1]. When two different drawings are included on one side of a sheet, the compositions are listed apart. The concentration of the others elements detected by PIXE or SR-XRF is not quantified because they were, in our mind, not included in the silver stylus used by Dürer (see below). n.q.: not quantified as below the limit of quantification.

Title	Museum*	Date	Part	wt.%	wt.%	wt.%	others
				Cu	Zn	Ag	
The town hall of Aix-la-Chapelle	Chantilly 893(316)r°	Oct. 1520		6.7	0.7	92.6	Hg
Portrait of Caspar Sturm	Chantilly 893(316)v°	Oct. 1520		6.0	0.3	93.7	Hg, Pb
Portrait of a person in front of St Michel d'Anvers abbey	Chantilly 892(315)r°	Nov. - Dec 1520		7.3	0.3	92.4	Hg
View of Bergen-op-Zoom	Chantilly 892(315)v°	beg. Dec. 1520		8.6	n.q.	91.4	Hg
A young and an old woman of Bergen-op-Zoom	Chantilly 891(314)r°	beg. Dec. 1520	young woman	8.4	0.7	89.9	Hg, Pb
			old woman	11.7	0.9	87.4	Hg, Pb
A young woman of Bergen-op-Zoom and a girl of Goes	Chantilly 891(314)v°	beg. Dec. 1520	woman	11.0	0.6	88.4	Hg, Pb
			girl	9.9	0.2	89.9	Hg, Pb
Lazarus Ravensburger and the tower of Liere	Berlin KdZ 35r°	Nov.- Dec. 1520	L. Ravensburger	5.3	n.q.	94.7	Hg, Pb
			tower	7.6	n.q.	92.4	Hg, Pb
Two girls	Berlin KdZ 35v°	beg. Dec. 1520	left girl	4.7	n.q.	95.3	Hg, Pb
			right girl	4.8	n.q.	95.2	Hg, Pb
Sitting bishop and portrait of a man with a fur cap	Berlin KdZ 34r°	March 1521	bishop	11.8	n.q.	88.2	Hg, Pb
			man with a cap	13.0	5.3	81.7	Hg, Pb
Two lions	Berlin KdZ 33v°	April 1521	left lion	5.7	n.q.	94.3	Hg
			right lion	3.4	n.q.	96,5	Hg
Lying dog, head of a dog and lion	Berlin KdZ 34v°	April 1521	lying dog	6.6	n.q.	93.4	Hg, Pb
			lion	3.7	n.q.	96.3	Hg, Pb
Portrait of a man and Krahenberg next to Anvers	Berlin KdZ 33r°	June 1521	portrait of a man	10.1	n.q.	89.9	Hg
			Krahenberg	12.4	n.q.	87.6	Hg
			signature	7.6	n.q.	92.4	Hg

* Chantilly = musée Condé, Chantilly, France

Berlin = Kupferstichkabinett, Staatliche Museen Berlin, Germany

Mercury was also detected in all drawings and is only located in strokes; this element has already been observed in metal point drawings other than made by Dürer [3]. Mercury was probably not included in the silver point when the drawing was made. On the one hand, experiments showed that silver amalgam could not be used for drawing; but on the other hand these experiments revealed that a contamination of silver point strokes by mercury was possible [3]. Even if this phenomenon could not be clearly

explained, we attribute the presence of mercury to a contamination from the atmosphere. Indeed, a large quantity of mercury has been liberated to the atmosphere mainly since the industrial period; and silver has a strong affinity to form a very stable amalgam with mercury. This formation seems to be a general alteration of the drawing silver alloy as it was observed on different drawings that were kept at various places.

Specifically the drawing of the *man with a fur cap* (from the drawing “*Sitting bishop and portrait of a man with a fur cap*”) presenting a high Zn content of the silver strokes also exhibits some lead point strokes. The origin of this drawing cannot be determined at the moment. Indeed, during restoration and fixation of the drawing in the mount, glues containing trace amounts of Zn are applied to strengthen or link the paper. Therefore, high Zn concentrations are found in the backing at the border of the drawings. However, this drawing was analysed at different points presenting the same Zn amount that was significantly different from that of the backing determined in positions next to the drawing and far from the border between drawing and mount. This led us to conclude that another silver point was used for the creation of this drawing.

On some drawings including the one mentioned before, lead was detected together with silver. The detection of this element can be explained by the presence of lead point strokes, which are visible under the microscope. These strokes are either a remain of a preliminary lead point sketch which was erased after the final silver point drawing was realised or correspond to some extra strokes added intentionally to the drawing in order to intensify its contrast.

Conclusion

This study shows that PIXE and SR-XRF are very useful to analyse metal point drawings. The results of analyses of silver alloy strokes made on paper are consistent with the results obtained by AAS analysis of the bulk. Applied to the study of Dürer's drawings from the sketchbook, PIXE and SR-XRF techniques give comparable results. Probably, Dürer used the same silver point during his travel in the Netherlands. Like in all previously analysed silver point drawings, mercury was detected in the drawings made by Dürer. The presence of this metal can most possibly be explained by a contamination. Further analyses are in progress in order to complete the actual database already including the works of Italian, Flemish and now German artists.

Acknowledgements

We gratefully acknowledge the help of H. Bevers, M. Roth, E. Alex and R. Wittich (Staatliche Museen Berlin, Kupferstichkabinett) as well as N. Garnier (musée Condé, Chantilly), for providing and accompanying the drawings for analysis. The reproduction of the A. Dürer drawing “*Sitting bishop and portrait of a man with a fur cap*” was provided by courtesy of the Kupferstichkabinett Berlin.

We are indebted to the accelerator team of the C2RMF for his valuable assistance. Sabine Schwertfeger is also thanked for running AAS analyses.

This work is supported, in the frame of a French-German project PROCOPE, by the German Academic Exchange Service (DAAD) under the contract number (D/0122896) and the French Foreign Office.

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