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PIXE measurements of Renaissance silverpoint drawings at VERA

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Abstract

Silverpoint drawings from the Renaissance are among the most precious and rarest treasures of graphical art. Our research group is particularly interested in the analysis of silverpoint drawings by Albrecht Dürer (1471–1528). A very sensitive and non-destructive analytical method, either spatially resolved synchrotron-radiation induced X-ray fluorescence (SY-XRF) or proton-induced X-ray emission (PIXE), is needed to determine the chemical composition of the very faint silver marks on such drawings. Dürer drawings from the collection of the Albertina, Vienna, were analyzed to amend existing data on Dürer drawings. For this purpose an external-beam PIXE setup was installed at the Vienna Environmental Research Accelerator (VERA). It allows to analyze a spot of ~0.15 mm on the object in air with 3 MeV protons, and to detect the emitted X-rays that are characteristic for the chemical composition with very good sensitivity and without harming the precious objects. After successful measurements on artificial test samples, four original silverpoint drawings were investigated: two portraits from Albrecht Dürer's very early period (self-portrait and portrait of his father) and two drawings from Dürer's sketch book of his travel to the Netherlands 1520/21.

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1. Introduction

The silverpoint is outstanding among the drawing materials used in the Renaissance like ink, black chalk and other metalpoints. Drawings made with a silverpoint are today considered some of the most precious treasures of graphical collections because of their quality and rarity as well as of the artistic technique requiring a great mastering for drawing. As only very few drawing instruments from this period are still existing, new insights are to be gained by analyzing the drawings themselves. The chemical composition will give details of the special type of graphical instrument used and may provide insight into the genesis of a drawing.

The drawings are generally executed on rag paper or parchment covered with a preparation layer mainly of bone white (a calcium phosphate) that may be colored with pigments. The metal particles deposited with a metalpoint on the drawing represent only some tens of μg per cm^2 (some tens of nm thickness). Former studies showed that only two analytical methods are both sensitive enough and non-destructive: external-beam proton-induced X-ray emission (PIXE) [1] and spatially resolved synchrotron-radiation induced X-ray fluorescence analysis (SY-XRF) [2].

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One of the most famous artists of the Renaissance who drew with silverpoint is Albrecht Dürer (1471–1528). Some of his silverpoint drawings are kept in the graphic collection of the "Albertina" in Vienna. Among them are:

(1) "Self-portrait at Thirteen" (Inv. No. 4839; the oldest preserved drawing of Dürer, dated by inscription to 1484).
(2) "Portrait of the Artist's Father, the Goldsmith Albrecht Dürer the Elder" (Inv. No. 4846; dated by art-historical observations to 1486).
(3) "Girl in Costume of Cologne; Agnes Dürer" (Inv. No. 22385r; dated according to Dürer's personal diary notes to 16.7.1521 [3]).
(4) "Lying Lion" (Inv. No.: 22385v; ditto dated to 10.4.1521 [3]).

The latter two are performed on both sides of a single sheet originating from the sketchbook that Dürer held during a travel to the Netherlands 1520/21.

First of all, our study intended to analyze the four drawings using a newly installed PIXE setup and to compare the chemical composition of these with other drawings by Dürer investigated earlier, i.e. with other drawings from the Netherlands sketchbook [1,2] and with one drawing from his early career, the portrait of "Willibald Pirckheimer" dated to 1503 [4]. Further insights into changes of the graphical technique of Albrecht Dürer in his life are expected by analyzing drawings from his very early period (1, 2) and those made at the end of his life (3, 4). It was also interesting to compare the drawing material used for the "Self-portrait at Thirteen" with those used for the "Portrait of the Artist's Father", attributed only two years later.

However, prior to the analysis of valuable art objects, the newly installed external-beam PIXE facility implemented at the Vienna Environmental Research Accelerator (VERA) had to be tested and validated for its capabilities to perform non-destructive, sensitive and quantitative chemical analyses. Therefore, preliminary test series helped to define adequate measuring conditions and to ensure the harmlessness of the experiment for these precious works of art. A full discussion supported by art-historical details is clearly beyond the scope of this paper. In the following we focus on the experimental setup, on the measurements and on the comparison of the analytical data with those of other Dürer silverpoint drawings [1,2,4].

2. Experimental setup at VERA

VERA is based on a 3-MV Pelletron tandem accelerator and was originally established as a general-purpose facility for accelerator mass spectrometry only [5]. In 2004, its capability was extended towards ion beam analysis to perform materials analysis by PIXE.

The PIXE setup used in our experiments is illustrated in Fig. 1. The exit tube for the proton beam is designed to optimize the target and detector geometry. For minimizing the beam diameter two carbon collimators are used: a 1.0 mm hole to ensure the correct direction of the beam, and a second one of about 120 μm to reduce the beam diameter. The transmission of the beam from the vacuum environment to atmosphere has to be through an ultra-thin

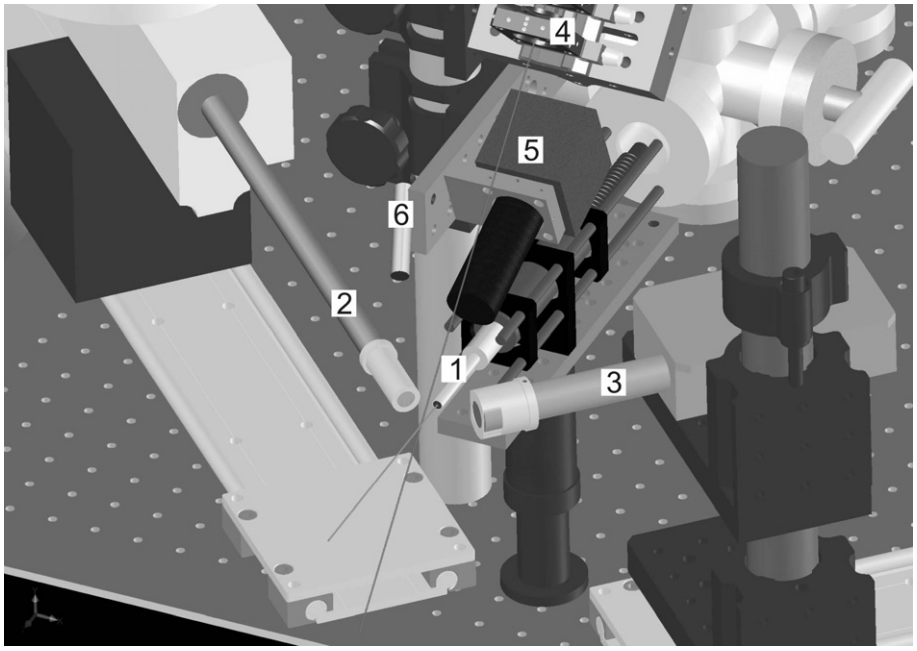

Fig. 1. CAD-drawing of the external-beam setup for PIXE at VERA. (1) Beam exit tube with collimating system and with Si_3N_4 exit window. The line indicates the green laser collinear with the proton beam. (2) 30 mm^2 Si (Li) detector with 150 μm Kapton window. (3) 100 mm^2 silicon drift detector with 150 μm Kapton window. (4) Red laser diode for positioning the specimen. (5) Firewire camera equipped with a macro lens. (6) Sub-miniature video camera.

window with the following constraints: (i) good mechanical resistance to withstand the 1 bar pressure-difference; (ii) minimum energy loss and minimum angular straggling; (iii) resistance to radiation damage; (iv) minimum background radiation [6]. We utilize a 100 nm Si_3N_4 membrane, $1.0 \times 1.0\ mm^2$ in size, framed by Si ($2.7 \times 2.7\ mm^2$, thickness 0.2 mm) [6]. The position of the sample was about 10 mm from the exit-window. There, the measured beam diameter is about 150 μm. To increase the solid angle for the detection of X-rays from the specimen we use two detectors: a Si(Li) with an active area of $30\ mm^2$ and a $100\ mm^2$ silicon drift detector. Both are mounted at an angle of 45° with respect to the incident beam and are about 20 mm from the beam spot on the sample for safety reasons. Kapton foils (150 μm thick) protect the detectors from backscattered protons and also reduce the high X-ray count rate from Ca in the low-energy part of the spectrum. A laser positioning system was implemented to select a measurement point on the drawing and to guarantee the very same detection geometry for each measurement. A green diode laser, aligned collinear with the proton beam, and a red diode laser at an angle of 45° with respect to the proton beam had to overlap on the surface of the investigated object. Sample positioning was performed by motor-driven stages moving in the plane perpendicular to the proton beam within a range of $350 \times 290\ mm^2$. The third axis allowed changing the distance from the exit window up to 290 mm. The stages were computer controlled with high resolution (~27 μm) matching the fine details (~200 μm) of silverpoint drawings. Four color cameras permitted to constantly monitor the specimen: A Firewire camera (resolution 1024×768 pixels) equipped with a macro lens resolved fine details of the object and was used to check if the positioning lasers were congruent. A subminiature video camera showed a larger section during positioning and the third camera gave an overall view of the whole setup. Additionally, high-resolution pictures from a digital camera (resolution 2592×1944 pixels) were taken before and after each measurement.

3. Systematic investigations on rag paper prior to the analysis of original drawings

Due to the high artistic value of original Dürer drawings and the premiere of such measurements at VERA, it was necessary to find optimum conditions with respect to analytical accuracy and minimum beam exposition [7]. Systematic tests with different papers were performed, in particular with modern printing paper and several ancient rag papers. Some of them were grounded with bone white or indigo, supposedly similar to the ground layer Dürer had used for his drawings. We varied proton energy, beam current and exposure time as well as the treatments after beam exposition. For the latter, the paper was subjected to accelerated ageing (described below), heating in dry air or exposing to extreme humidity. Proton irradiation was within typical conditions for PIXE analysis, and also largely exceeding them (tens of pA up to tens of nA). Areas with extremely high doses developed brown or even black spots instantly during exposure. Below about 10 nA of 3 MeV protons and exposure times of about 300 s no effect became immediately visible. To observe the development of beam damage after "long time", several papers underwent accelerated ageing. The accelerated ageing process is divided into cycles; each one lasts 3 h. During a cycle relative humidity started at 30%; after about 15 min it was set to 90% for about 1 h and then to 30% again. Temperature was constantly at about 80 °C. One hundred of such cycles correspond to an ageing of approximately 100 years [8]. We could show [7], cf. Fig. 2, that with standard measuring

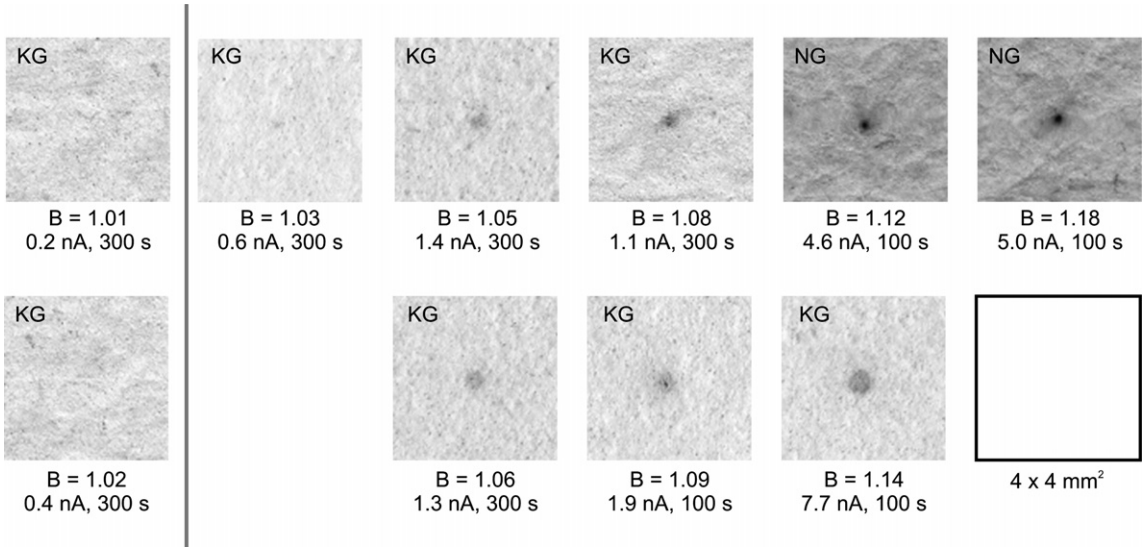

Fig. 2. Enlarged images of irradiated paper areas after accelerated ageing, ordered by increasing exposure to protons. NG is ungrounded rag paper, KG is grounding with bone white. The so-called black-value B (essentially the ratio between the gray-scale values of a spot and its environment) indicates the amount of beam-induced discoloration. For the left most figures with B up to 1.02, separated from the rest by a vertical line, no effect is visible.

conditions (~0.3 nA of proton current, 3 MeV proton energy and 300 s irradiation time) no effects were visible even after accelerated ageing equivalent to "some hundred years". It is important to mention that the parameters are only relevant for the experimental situation at VERA. This applies in particular to the proton currents stated here, since current measurements are notoriously difficult in air [9].

4. Analysis of silverpoint drawings

Since the four original drawings were not solely executed with a silverpoint, areas of interest were selected by investigation under an optical microscope prior to PIXE analysis. For example, the inscription and some small parts of the face of "Self-portrait at Thirteen" seem to have been carried out with ink.

For each drawing up to 20 points on the silver marks were analyzed. To obtain the chemical signature of the silverpoint we normalized the major elements Ag, Cu and Zn in each mark relative to MicroMatter standard materials. Elemental ratios were calculated by assuming Cu + Zn + Ag = 100%. During all measurements also a significant amount of ground layer and rag paper is exposed to the proton beam. Cu and Zn impurities contained there have to be subtracted. Consequently, up to 10 points on the background were measured for each drawing. Further elements in the ground layer or in the paper such as Fe and Sr need not to be considered for quantitative evaluation of the silver alloy. It should be mentioned, that the uncertainties for the single measurements are relatively large because of the intrinsic inhomogeneity of the sample, i.e. the paper, and the ground layer.

We also observed the presence of Hg in the silver marks. As proven earlier [10], the Hg content is due to absorption from air, an alteration in the course of time, and, thus, Hg was not included into the quantification of the silver marks.

5. Results and discussion

All analytical data for the PIXE measurements at VERA are summarized in Table 1. The "Self-portrait at Thirteen" is grounded with a white preparation layer, most probably made of bone white (see also [1]). The very low Pb content indicates a possible small addition of lead white. We could confirm that for most parts of the drawing a silverpoint with an average composition of (7.8 ± 2.7) wt.% of Cu, (0.9 ± 0.8) wt.% of Zn and (91.3 ± 3.2) wt.% of Ag was used. The inscription of the drawing and some small parts of the face seem to be carried out with iron gall ink. Interestingly, one of the three measuring points in the inscription (in the "h" of Albrecht) unexpectedly contains silver, whereas in the other two points no silver was found. Since this mark shows the same composition as in the portrait, it could be an underlayer of the ink, and the original inscription might have been overwritten.

The ground layer of the "Portrait of the Artist's Father" reveals to be a mixture of bone white and lead white, but is drastically different in its aspect and composition from the "Self-portrait at Thirteen" and the drawings from the sketchbook. In Fig. 3 the various L-lines of Pb are clearly visible. They are about 500 times more intense than for all other analyzed drawings. The silver marks analyzed in the "Portrait of the Artist's Father" basically contain (9.2 ± 2.6) wt.% of Cu, (1.0 ± 1.1) wt.% of Zn and (89.8 ± 3.2) wt.% of Ag. Because of the very strong presence of Pb, Hg cannot be unambiguously identified. Four out of 15 measurement points scattered across the portrait have a different composition of the silver alloy: (17.1 ± 3.5) wt.% of Cu, (3.5 ± 2.3) wt.% of Zn and (79.4 ± 4.6) wt.% of Ag. This may indicate the use of a second silverpoint, but there are too few measurement points to fully exclude effects due to inhomogeneities. Pb is not only present in the ground layer but also in some parts of the drawing. This raises the question of the drawing technique. Either gouache or leadpoint could explain the extraordinary high Pb signal for three particular measuring points. The complexity of the drawing materials and of the drawing technique found for the "Portrait of the Artist's Father" call for further analysis.

The drawing "Girl in Costume of Cologne; Agnes Dürer" shows a silverpoint containing (6.5 ± 1.4) wt.% of Cu, (0.5 ± 0.5) wt.% of Zn and (93.1 ± 1.5) wt.% of Ag. A typical PIXE spectrum can be seen in Fig. 3. It also indicates an excess of Hg in the silverpoint marks as compared to the ground layer. For the ground layer the very low Pb content together with a high Ca content point to the use of bone white, with possibly a small addition of lead white. Three measured points out of 11 show a high Zn content (3.2 ± 0.7) wt.% and a high Cu content (12.0 ± 0.4) wt.%. Because of this distinctly different composition we did

Table 1
Results of silverpoint drawings analyzed at VERA

Drawing	wt.% Cu	wt.% Zn	wt.% Ag	Hg
Self-portrait at Thirteen	7.8 ± 2.7	0.9 ± 0.8	91.3 ± 3.2	Clearly present
Portrait of the Artist's Father, the Goldsmith Albrecht Dürer the Elder	9.2 ± 2.6	1.0 ± 1.1	89.9 ± 3.2	Unclear due to Pb from backing
Girl in Costume of Cologne; Agnes Dürer	6.5 ± 1.4	0.5 ± 0.5	93.1 ± 1.5	Clearly present
Lying Lion	8.4 ± 1.4	0.4 ± 0.8	91.2 ± 1.2	Clearly present

Concentrations are given in wt.% with Cu + Zn + Ag = 100%. The uncertainties represent variations in e.g. measurement condition, inhomogeneous ground layer, etc. Other elements like Hg from alteration [10] are not taken into account. Mean values are taken over the particular drawing.

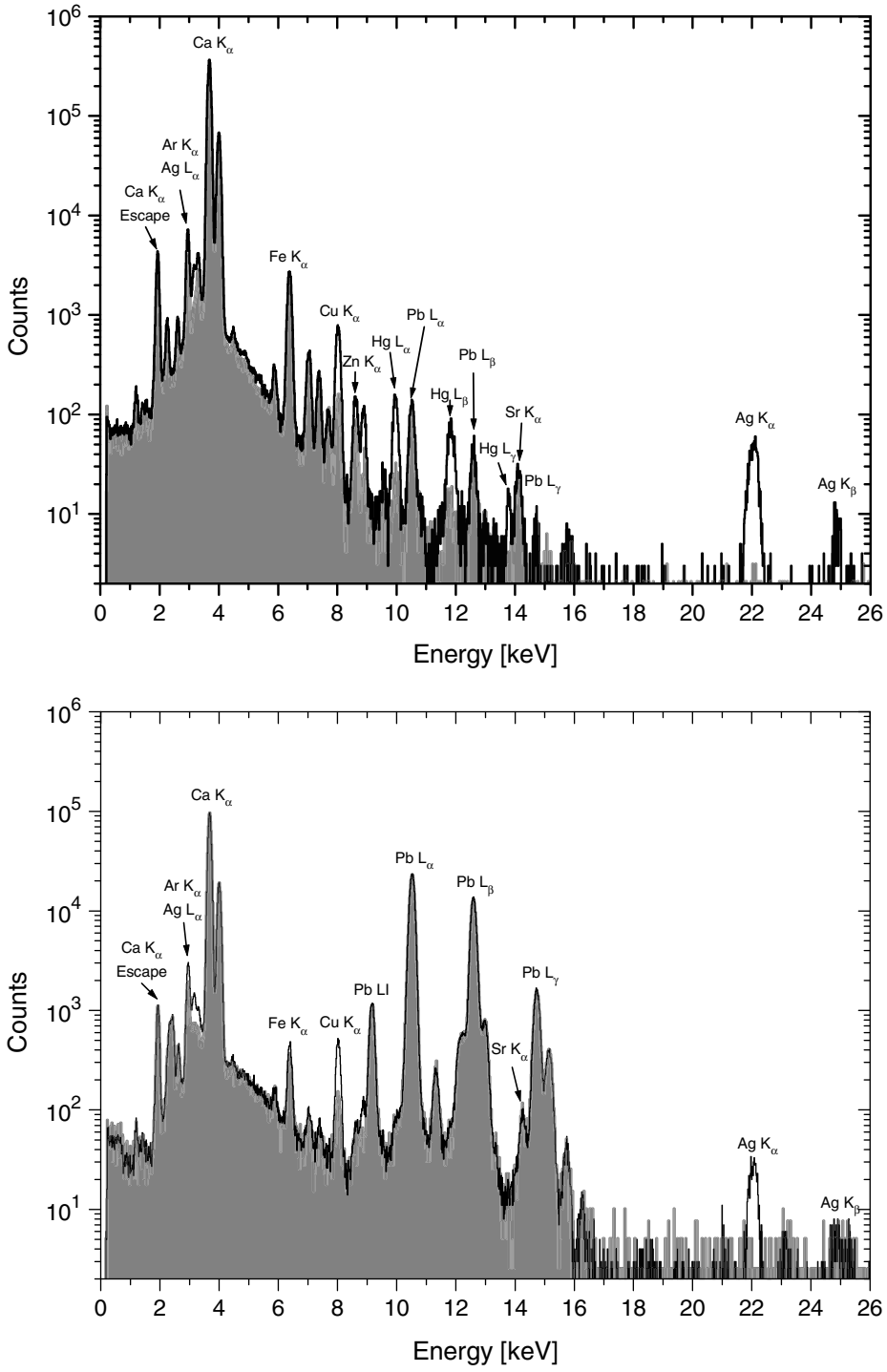

Fig. 3. PIXE spectra from (upper panel) "Girl in Costume of Cologne; Agnes Dürer" and (lower panel) "Portrait of the Artist's Father, the Goldsmith Albrecht Dürer the Elder" acquired with a Si(Li) detector. The thick line is from the silverpoint marks; the shaded area is from the ground layer only.

not include them in the evaluation. On the other hand, they are not significant enough to conclude about a possible second silverpoint.

All eight analyzed marks from "Lying Lion" – the verso of the above sketchbook sheet – yield a composition of (8.4 ± 1.4) wt.% of Cu, (0.4 ± 0.8) wt.% of Zn and (91.2 ± 1.2) wt.% of Ag with small amounts of Hg.

The range of values found in our study is consistent with the previous investigations on the other drawings from Albrecht Dürer's sketchbook of his journey to the Netherlands 1520/21. The sketchbook was split in the late 19th century. Twentyseven drawings, well-documented in Dürer's diary are now conserved in different art collections. Some of these drawings have already been investigated: six drawings were analyzed by PIXE at Paris [1], and nine more by SY-XRF at Berlin [2]. In the right part of Fig. 4 we compare our new PIXE results from VERA for "Girl in Costume of Cologne; Agnes Dürer", and "Lying Lion"

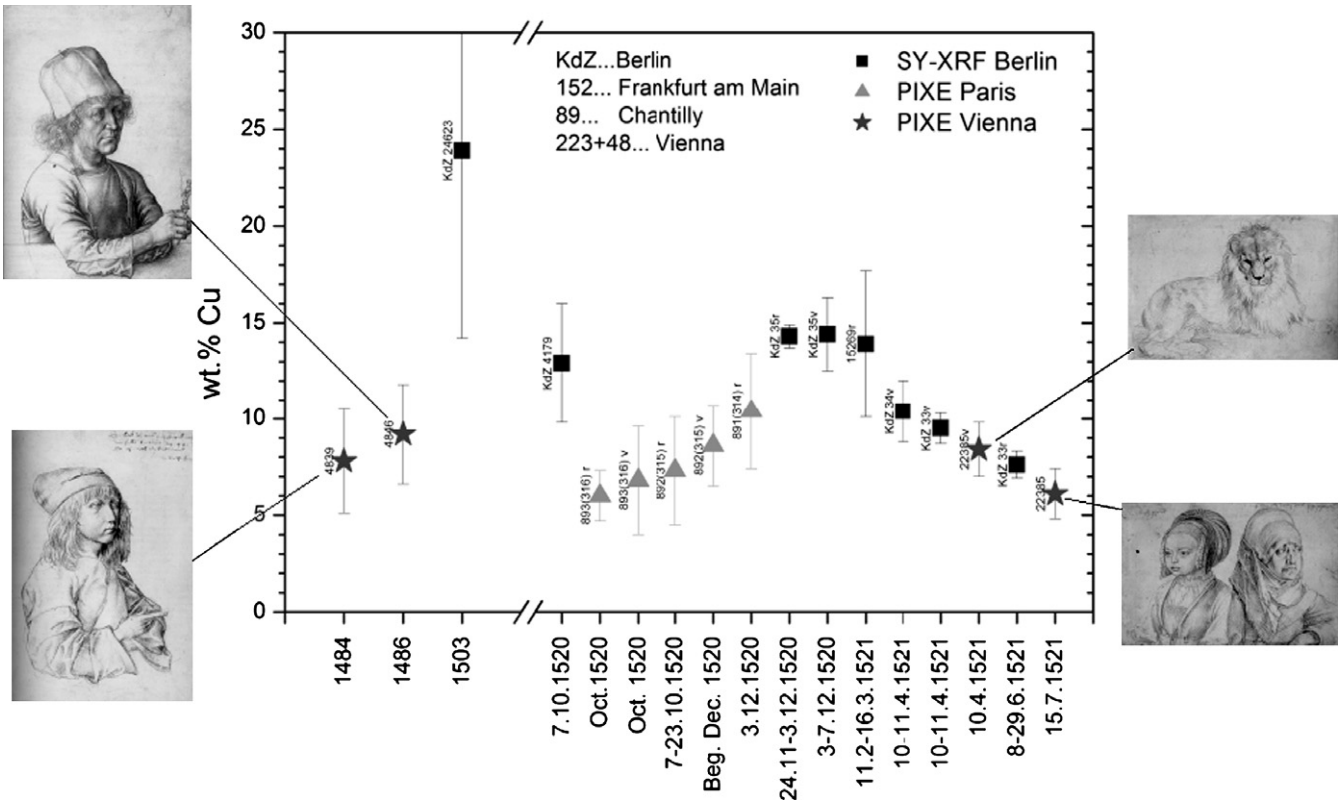

Fig. 4. Copper content of silverpoint drawings by Albrecht Dürer. The abscissa shows the dates of the drawings; their inventory number is given beside the data. Results from the present work are plotted with star symbols; previous data by SY-XRF [2] and by PIXE [1] are marked with rectangles and triangles, respectively. The pictures show the drawings measured in the present work (clockwise from left bottom): "Self-portrait at Thirteen", "Portrait of the Artist's Father, the Goldsmith Albrecht Dürer the Elder", "Lying Lion", "Girl in Costume of Cologne; Agnes Dürer".

to previous measurements on other drawings from the sketchbook. All results are arranged in chronological order. The results of the newly analyzed drawings fit nicely into the overall picture and support the perception that all drawings of the journey to the Netherlands described in the diary were made with the same kind of silverpoint. The mean value of Cu in the silver marks averaged over all drawings analyzed up to now is (10.6 ± 3.5) wt.%. Sometimes, traces of Zn in the order of 1% were found. The apparent chronological variation in the Cu content remains so far unexplained.

In the left part of Fig. 4 we compare early silverpoint drawings from Albrecht Dürer. Of particular interest is the comparison of the silverpoint used for "Portrait of the Artist's Father" and the "Self-portrait at Thirteen". From the analytical data we have no reason to assume the use of different silverpoints. Our measurements not only yield a very similar composition in these early drawings, it is also strikingly similar to the silver alloy used in the later work of 1520/21. Obviously, the silverpoint used in "Willibald Pirckheimer" (1503) shows an exceptionally different Cu concentration [4].

6. Conclusions

Our results of the sketchbook drawings "Girl in Costume of Cologne; Agnes Dürer" and "Lying Lion" support earlier assumptions [2] that the drawings from Dürer's sketchbook 1520/21 were made with one type of silverpoint. Including the similar results of "Self-portrait at Thirteen" and "Portrait of the Artist's Father", we obtain an overall Cu content of (10.1 ± 3.1) wt.% for the silver alloy, and a low content of Zn (<1 wt.%).

Concluding, we have successfully applied the sensitive and non-destructive method of PIXE to analyze very precious objects of fine arts. Thus, the PIXE setup at VERA opens new perspectives for art-historical investigations, particularly for Austrian museums as it is the only external-beam PIXE facility in Austria. In general, it offers opportunities for studies of cultural heritage which becomes a focus of research at the European level.

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