

# Mössbauer Study of Iron Gall Inks on Historical Documents

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# Mössbauer study of iron gall inks on historical documents

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## Abstract

Iron gall ink was used as a permanent writing material already in late Roman times and throughout the Middle Ages, until it became obsolete in the 20<sup>th</sup> century. There is much interest in non-destructive experimental methods to determine the state of the ink and its degradation products on historical documents. Mössbauer spectroscopy is such a method, and it has the particular advantage to be sensitive to the chemical bonding of iron, but this method has only rarely been applied to historical documents. In this paper we present Mössbauer data for two damaged documents from a Library in Granada and a handwritten German book from the 18<sup>th</sup> century. These new results are discussed in the context of previously published Mössbauer data. In one of the investigated documents Fe-(II)-oxalate,  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , was observed. The assignment of the various  $\text{Fe}^{3+}$  sites in the different documents is rather difficult and often there is a superposition of various species. These species can be remains of the Fe-tannin complexes of the ink, complexes of  $\text{Fe}^{3+}$  with the cellulose of the paper and different iron oxide or hydroxide nanoparticles.

## Introduction

Iron gall inks were already used in late Roman times [1] and became the most important writing material in the Middle Ages and during modern times until they became obsolete in the 20<sup>th</sup> century. Documents written with such inks often suffer from severe degradation, depending on the quality of the papers and on the composition of the ink [2, 3]. The chemical nature of the color-carrying component and the processes of degradation are still a matter of

debate [3]. In the past decades, there has been a growing interest in addressing these questions by physical methods that allow non-destructive investigations, sometimes with a high spatial resolution. Proton induced X-ray spectroscopy (PIXE) [4-6] and X-ray fluorescence spectroscopy (XRF) [1, 7-11] allow a quantitative analysis of the various elements in written documents on a scale of 0.5 to 3 mm. Attenuated total reflectance (ATR), Fourier transformed infrared (FTIR) [7-9] and micro-Raman spectroscopy [1, 7-9, 12, 13] give information on the chemical nature of the organic compounds involved in ink formation and their degradation products. Only micro-XANES (X-ray absorption near edge spectroscopy) [11, 14] and Mössbauer spectroscopy [15-18] with  $^{57}\text{Fe}$  are sensitive to the chemical state of the iron, which is thought to be the essential component of the color-carrying unit and perhaps an important player in the degradation processes. Whereas XANES monitors mainly the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, Mössbauer spectroscopy additionally allows more detailed conclusions on the chemical state of the iron on the basis of the isomer shift and quadrupole splitting, and it allows the identification of magnetically ordered phases like iron oxides or hydroxides. In principle, Mössbauer spectroscopy is non-destructive, but it requires relatively large amounts of material. Up to now only a few documents have been investigated by Mössbauer spectroscopy: Ancient manuscripts studied by Mössbauer spectroscopy are a French document from the 15<sup>th</sup> century [15, 16], a Syriac document from the 12<sup>th</sup> century [15], and three documents from the national library of Poland [17]. More recently, Mössbauer spectroscopy also revealed the presence of traces of iron in the paper of old documents [18].

In this paper Mössbauer data are presented for two document fragments from the University Library in Granada (Spain) and for a German hand-written cookbook from the 18<sup>th</sup> century. Measurements were performed at both ambient temperature and at 4.2 K. Care was also taken to study the paper on which the documents were written for traces of iron. The new results are discussed in the context of the previous Mössbauer data. In one of the Spanish documents, Fe(II)-oxalate ( $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) was observed, which apparently is a deterioration product of the cellulose. The assignment of the various  $\text{Fe}^{3+}$  sites observed in the different historical documents is not straightforward. Iron oxides or oxy-hydroxides can be identified by Mössbauer measurements at liquid helium temperature, where they are magnetically ordered. Species that are still paramagnetic at 4.2 K, however, are difficult to identify. It is difficult to decide whether they are remains of iron tannin complexes of the ink or iron-cellulose adducts.

## **Experiments and methods**

### *1. Historic documents and absorber preparation*

Two of the studied documents were parts of single pages provided by T. Espejo, Granada. Both were endpapers of a book printed in Rome in 1715 and were removed from that book in the course of a recent restoration carried out in Granada. The manuscript shown in Fig. 1a is written in a chancery hand called *letra procesal*. This type of writing was used in Spain in the 15<sup>th</sup> and 16<sup>th</sup> century. We will call this specimen *Chancery MS* in the following. The writing on it is rather irregular, indicating that it was written as a calligraphic exercise. The writing is grayish and faded, and the paper turned out to be quite brittle. After removal of the rim not containing any ink, the remainder was therefore crushed and put into a Lucite absorber holder. The rim was also put into an absorber holder for separate measurements of the paper alone. The manuscript shown in Fig. 1b consists of rather large single letters in Latin script, probably also from a calligraphic exercise, and will be called *Latin MS*. In this case it was possible to cut the deep black letters out of the manuscript to be studied separately from the parts that did not contain any ink. Both the ink-covered part and the remainder were put into Lucite sample holders for Mössbauer measurements at RT and 4.2 K. The thicknesses of the individual absorbers are given in Table 1.

The third historic document we investigated is the handwritten cooking book of a lady, Anna Maria Widenplazerin, from the year 1783 (private property of F.E. Wagner, Fig. 2). This book is quite well preserved, but the writing is rather faint and brownish. For a Mössbauer measurement at room temperature (RT), the 14.4 keV gamma rays were passed through 53 pages of the opened book, which yielded a good Mössbauer transmission spectrum within a few days. For a low temperature measurement we had to remove a page from the book. This was cut into squares of about 15 x 15 mm<sup>2</sup>. Of these, 121 were stacked to make a Mössbauer absorber, which was measured at both 4.2 K and RT. In order to check whether there is any iron in the paper itself, we also removed an empty page from the book and cut it into squares, from which a Mössbauer absorber consisting of 88 layers was made and measured at RT and 4.2 K.

For comparison with components in the document samples, we measured Mössbauer spectra of Fe(II)-oxalate obtained commercially from Alpha and hydronium jarosite, which we obtained by letting a hydrous solution of FeSO<sub>4</sub>·7H<sub>2</sub>O dry in a flat dish at about 20 °C within a few weeks.

## 2. Methods

The room temperature Mössbauer spectra were recorded with a conventional transmission spectrometer using a sinusoidal velocity waveform (Halder Elektronik, Germany) and a ca. 25 mCi source of  $^{57}\text{Co}$  in Rh. Low temperature measurements were performed in a liquid He bath cryostat with both source and absorber cooled to 4.2 K. The 14.4 keV gamma rays of  $^{57}\text{Fe}$  were detected with a Kr/CO<sub>2</sub> filled proportional counter. Isomer shifts (IS) are given with respect to the source having the same temperature as the absorber and can be converted to shifts relative to  $\alpha$ -iron at room temperature by adding 0.11 mm/s to the room temperature data. To the 4.2 K data, 0.24 mm/s have to be added to refer them to  $\alpha$ -iron at room temperature, because the second order Doppler shift has to be taken into account. All spectra were least-squares fitted with superpositions of Lorentzian lines grouped into quadrupole doublets or magnetically split sextets. In a few cases, Gaussian distributions of hyperfine fields gave better fits for magnetically split patterns than sextets with Lorentzian lines. In such cases a Lorentzian width of 0.25 mm/s was used and the distributions are described by the mean field  $B$  and the variance  $\sigma_B$  of the field distribution. The line-shapes were calculated by superimposing 40 sextet patterns with Lorentzian line-shapes, different hyperfine fields and appropriate intensities.

The surface pH was measured with a Mettler Toledo Seven Easy instrument and a Metrohm Nr. 6.0256.100 surface electrode at spots with and without visible ink. The measurements were carried out according to the TAPPI-protocol T 529. For the measurement the paper was placed on a flexible, hydrophobic support pad. De-ionized water (0.05 ml) was applied to the position selected for measurement. The glass electrode mounted in a support was then carefully placed on the drop of water and pressed onto the paper surface to make good contact. The measurement stopped automatically after equilibrium was reached. IR-spectra were measured with a Bio-Rad FTS 575CIR spectrometer equipped with a Pike Technologies MIRacle ATR unit. A visual coloring test with zinc chloride-iodide [19] expectedly showed that all three papers under investigation are of rag-type, probably from flax and hemp.

## Results

### *Iron contents of the samples*

The Mössbauer spectra of the studied documents are shown in Figures 3, 4, and 5. On the left side of these Figures, the spectra of the papers with writing on them are shown. To make certain that these spectra really represent the traces of the ink on the papers and not merely an iron contamination of the papers themselves, we measured Mössbauer spectra of pieces of all three documents which are free from visible traces of ink. These are shown on the right side of Figures 3, 4, and 5. It turns out that all three papers contain some iron, but at least a factor of ten less than for the pieces with writing.

The fitting results of the Mössbauer spectra are summarized in Tables 1 and 2. Table 1 gives the thickness of the absorbers and the total area under the Mössbauer spectra at 4.2 K and RT calculated by the fitting procedure as the product of the fractional depth and the width of the individual lines in the spectra and summed over all lines. Table 2 gives the hyperfine parameters obtained for the individual components obtained from the least squares fits of the Mössbauer spectra.

From the spectral areas given in Table 1 one can estimate the area density of iron in the absorbers, and hence the iron content per unit mass of the absorber material. For this, separate reference measurements with a hematite absorber of known thickness were taken under similar conditions as for the measurements of the documents. Assuming that the Lamb-Mössbauer  $f$ -factors of all components in the spectra of the documents are the same as that of hematite, one can then obtain the iron contents of the document samples. The iron contents obtained in this way are also given in Table 1, as are the measured pH values of the papers. The main uncertainty in the determination of the iron contents of the document samples results from the assumption of equal  $f$ -factors for the hematite reference and the iron species on the papers. Since hematite has one of the largest  $f$ -factors known for iron compounds and other iron oxides and oxy-hydroxides have similarly high  $f$ -factors of about 0.9 at 4.2 K and 0.85 at RT [20, 21], the uncertainty should be no more than about 5 per cent if all iron was present in the documents as oxides or oxy-hydroxides. Iron compounds with organic ligands, however, may have substantially lower  $f$ -factors, which are also expected to decrease more strongly with increasing temperature. The iron content of the samples from the documents as given in Table 1 may thus be underestimated, depending on what the iron species in the individual cases are. This will affect the iron contents obtained from the RT spectra more than those obtained from the 4.2 K data, since the  $f$ -factors for materials with lower  $f$ -factors at 4.2

K also decrease more strongly at higher temperatures. The generally lower iron contents of the papers with writing at RT compared to 4.2 K (Table 1) therefore indicate a substantial decrease of the f-factors of the iron species with increasing temperature. As an example, and because iron oxalate is the only iron phase with organic ligands that could be unambiguously identified in one of the documents, we have measured the f-factors of Fe(II)-oxalate at 4.2 K and at room temperature by a direct comparison with a foil of  $\alpha$ -iron, making an absorber containing known amounts of both substances simultaneously (5,68 mg/cm<sup>2</sup>  $\alpha$ -Fe, 21.5 mg/cm<sup>2</sup> FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O). With  $f(4.2\text{ K}) = 0.925$  and  $f(300\text{ K}) = 0.80$  for  $\alpha$ -Fe [22] one thus obtains  $f(4.2\text{ K}) = 0.75$  and  $f(300\text{ K}) = 0.34$  for the oxalate.

The iron contents of the papers with writing obtained from the room temperature spectra are generally lower by about a factor of two than those obtained from the 4.2 K spectra, which indicates that much of the iron is mainly bound to organic ligands. For the iron in the paper itself, roughly the same iron contents are obtained from the room temperature and 4.2 K measurements. This indicates that the iron in the papers is present largely as oxidic phases whose f-factors change with temperature much like that of hematite. In the case of the paper of the cookbook, the determination of the iron content from the 4.2 K spectra is subject to a considerable uncertainty because, due to the low iron content, the intensity of the magnetically split pattern at 4.2 K is subject to a large statistical uncertainty. It is clear, however, that all papers contain about a factor of ten less iron than the parts with writing. In the following discussion of the ink spectra, it therefore appears justified to neglect the influence of the iron in the papers.

With 21 mg/g, the parts with writing of the *Latin MS* contain more iron than the *Chancery MS* (6 mg/g), probably because the large letters in the *Latin MS* could be cut out with very little ink-free paper adhering, which was not the case for the *Chancery MS*. The cookbook contains much less iron than the *Chancery MS*.

#### *Mössbauer spectra of the papers with applied ink*

Table 2 gives the hyperfine parameters obtained for the individual components obtained from the least squares fits of the Mössbauer spectra. The RT spectrum of the *Chancery MS* (Fig. 3, top left) is dominated a ferrous quadrupole doublet with  $QS = 1.73$  mm/s,  $IS = 1.09$  mm/s and 42 % of the spectral area. The ferric component making up the rest of the spectrum required two quadrupole components for a satisfactory fit, namely a doublet with rather narrow lines,

17 % of the area and an uncommonly large QS value of 1.23 mm/s. and a broad doublet making up the remainder of the spectrum. This broad doublet probably represents different species, whose individual contributions cannot be resolved.

In the rather complicated 4.2 K spectrum (Fig. 3, bottom left) the dominant Fe<sup>2+</sup> component exhibits a magnetic hyperfine splitting into an octet pattern, as is expected for ferrous iron in magnetically ordered substances [23]. This octet could be fitted with a hyperfine field of B = 15.3 T, a quadrupole interaction of QS = -1.96 mm/s, and an asymmetry parameter of the electric field gradient of  $\eta = 0.68$ . One should note that the octet pattern allows the sign of the electric quadrupole interaction to be determined, while from the doublet observed at RT only the magnitude of QS can be obtained. For the angles defining the direction of the hyperfine field in the coordinate system of the electric field gradient [23], values of  $\theta = 90^\circ$  and  $\varphi = 0^\circ$  were assumed and fixed during the least squares fit. This Fe<sup>2+</sup> component is very similar to one observed in a degraded document by Danon et al. [15], who assigned it to hydrated Fe(II)-oxalate, FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. RT and 4.2 K spectra taken of a commercially obtained Fe(II)-oxalate (Fig. 6, top, and Table 1) are in good agreement with the Fe<sup>2+</sup> sites in the *Chancery MS* and with published spectra of iron oxalate [24, 25].

The narrow quadrupole doublet of the Fe<sup>3+</sup> component with QS = 1.23 mm/s in the room temperature spectrum of the *Chancery MS* splits at 4.2 K into a magnetic sextet that can be fitted with a magnetic hyperfine field of B = 47.8 T, a quadrupole shift of QS = -0.12 mm/s and an IS of 0.26 mm/s (Table 1). These parameters are in good agreement with published data for hydronium jarosite (H<sub>3</sub>O)Fe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> [26, 27] and with the fitting data of the Mössbauer spectrum of a sample of hydronium jarosite, which was obtained by allowing an aqueous solution of Fe(II)-sulfate to evaporate to dryness at RT within a few weeks (Figure 6, bottom, and Table 1). The spectra of the dried solution of ferrous sulfate still contain a weak ferrous quadrupole doublet that cannot be assigned to a ferrous sulfate. Surprisingly, the relative intensities of the doublets obtained at RT for Fe(II)-oxalate and jarosite (42 and 17 %, respectively, Table 1) are nearly the same as those obtained for the magnetically split spectra at 4.2 K (42 and 23 %, Table 1). This suggests that the f-factor of jarosite decreases with increasing temperature in similar way as that of Fe(II)-oxalate. We have therefore measured it in the same manner as that of Fe(II)-oxalate and obtained for a potassium jarosite prepared in a similar manner as described by Majzlan et al. [28]  $f(4.2 \text{ K}) = 0.86$  and  $f(300 \text{ K}) = 0.45$ , i.e., also a decrease of about a factor two between 4.2 K and 300 K.

In the RT spectrum of the *Chancery MS* a second broad  $\text{Fe}^{3+}$  doublet with a quadrupole splitting of  $QS = 0.84 \text{ mm/s}$  and a fractional area of 41 % is needed to obtain a good fit. At 4.2 K a rather strong ferric doublet (23 %) with  $QS = 0.83 \text{ mm/s}$  is still present, but an additional weak (7 %) magnetic sextet with a hyperfine field of 53.7 T is observed. The high hyperfine field of this sextet indicates that it is caused by slow paramagnetic relaxation of isolated  $\text{Fe}^{3+}$  ions. Apparently, part of the iron species that give rise to the broad ferric doublet in the RT spectrum split magnetically in this way at 4.2 K, while the rest remains a quadrupole doublet. This indicates that there are two different iron species, of which only one shows slow paramagnetic relaxations. The fit also requires an additional minor (9 %)  $\text{Fe}^{2+}$  doublet. For fitting this, the isomer shift was restrained to a value typical for iron with six  $\text{H}_2\text{O}$  ligands. Then a quadrupole splitting of  $QS = 2.75 \text{ mm/s}$  is obtained. A similar doublet is not visible in the room temperature spectrum, probably because the f-factor of this species is too low.

The room temperature Mössbauer spectrum of the *Latin MS* (Fig. 4, top left) exhibits only one  $\text{Fe}^{3+}$  doublet with  $QS = 0.79 \text{ mm/s}$  (Fig. 4, bottom left). At 4.2 K there is still a ferric quadrupole doublet with practically the same  $QS$  making up about 60 % of the spectral area. The remainder splits magnetically into a broad pattern suggesting slow and intermediate paramagnetic relaxations of ferric ions. In the fit, this pattern was approximated by two static Gaussian distributions of hyperfine fields. A minor fraction of the spectral area (6 %) of the iron can be represented by a rather narrow distribution around a mean field of 52.1 T with a variance of  $\sigma_B = 3.2 \text{ T}$ , while the remainder can be fitted with a very broad distribution of hyperfine fields around a mean value of 26 T with a variance of  $\sigma_B = 20 \text{ T}$ .

Superparamagnetic relaxation of oxidic nanoparticles appears to be improbable at 4.2 K. The broad magnetically split patterns therefore rather seem to be due to slow and intermediate paramagnetic relaxations of individual  $\text{Fe}^{3+}$  species. In the 4.2 K spectrum there is also a very weak ferrous doublet, which gives rise to a small bulge at about +2.5 mm/s. The location of the second component of this doublet cannot be seen below the strong ferric doublet. The parameters of this component therefore had to be fixed to plausible values in the fit and must be considered as rough approximations.

The RT Mössbauer spectrum of the cookbook (Fig. 5, top left) exhibits only a ferric quadrupole doublet with a quadrupole splitting of 0.77 mm/s. The 4.2 K spectrum (Fig. 5, bottom left) is still dominated by a ferric quadrupole doublet with 24 % of the area, but the remainder of the iron exhibits magnetic hyperfine interactions. One can distinguish three

patterns, which were all fitted with Gaussian distributions of hyperfine fields. Of these, the rather clearly defined sextet with  $B = 44.9$  T and  $\sigma_B = 2.8$  T can tentatively be assigned to lepidocrocite ( $\gamma$ -FeOOH) [29, 30], perhaps as small particles causing the line broadening. Lepidocrocite is paramagnetic at RT and orders magnetically below about 70 K [26]. The other two components are similar to those found in the *Latin MS* at 4.2 K and can be explained in the same way as arising from too slow paramagnetic relaxations.

#### *Mössbauer spectra of the papers without ink*

The room temperature (Fig. 3 - 5, top right) as well as the 4.2 K spectra (Fig. 3-5, bottom right) of all papers are dominated by a ferric quadrupole doublet with a splitting of about 0.8 mm/s. In the low temperature spectra of all three papers (Fig. 3, 4, 5, bottom right) at least one sextet due to magnetic hyperfine splitting appears. The paper of the *Latin MS* exhibits a weak magnetic sextet already at RT. According to its hyperfine parameters (Table 1) this can be attributed to hematite. At 4.2 K, the hematite is still visible with a hyperfine field of 53.3 T. It does not undergo the Morin transition, which shows that it is present as rather small or badly crystallized particles. An additional magnetic component with rather broad lines in the 4.2 K spectrum of the paper of the *Latin MS* was fitted with a Gaussian distribution of hyperfine fields ( $B = 49.7$  T and  $\sigma_B = 2.4$  T). These hyperfine parameters suggest that this component may represent small goethite particles that exhibit only a quadrupole doublet at RT because of superparamagnetism but split magnetically at 4.2 K [31, 32]. The 4.2 K spectrum of the paper of the cookbook also seems to contain a magnetically split pattern, but the bad statistical accuracy of the spectrum makes it impossible to give details of this. In the RT spectrum of the paper of the *Chancery MS* (Fig.3, top right) a weak ill-defined ferrous doublet seems to be present, which is hardly visible at 4.2 K. In the paper of the *Latin MS*, a minor amount of ferrous iron is definitely present. In the paper of the cookbook, no ferrous iron can be seen.

#### *Infrared spectra*

Since the presence of Fe(II)-oxalate hydrate has been discovered in historical documents [33, 34] and old papers soaked with FeCl<sub>3</sub> [35] by means of IR spectroscopy, IR spectra of the *Latin MS* as well as the *Chancery MS* were measured. Fig. 7 shows the attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra of both samples for spots with ink and for ink-free paper. All four spectra look quite similar and correspond quite well to the IR spectrum of cellulose [36]. In case of the *Latin MS* there is hardly any difference between

the spectra of the black ink spots and the ink free paper. The spectrum of the ink spot of the *Chancery MS* shows two significant variations with respect to the spectrum of the ink free paper, One is that a signal at about  $1430\text{ cm}^{-1}$ , which is also present in the cellulose spectrum and there ascribed to -C-H vibrations, gains strongly in intensity. In the IR spectra of various samples in the papers of Ferrer and Sistach [33, 34] there is also a pronounced peak at about  $1400\text{ cm}^{-1}$ , but the authors assign it to Fe(III) potassium oxalate and/or to ammonium iron(II) sulfate. These assignments are not possible for our *Chancery MS*, because there is no evidence for these compounds in the Mössbauer spectra. The other difference in the IR spectra with and without ink is a weak signal at about  $814\text{ cm}^{-1}$  that could be a hint to the Fe(II)-oxalate hydrate [33, 34]. The other three signals of the ferrous oxalate at  $1628\text{ cm}^{-1}$ ,  $1358\text{ cm}^{-1}$  and  $1316\text{ cm}^{-1}$  cannot be distinguished from signals of the cellulose [36].

## Discussion

### *Papers with applied ink*

Leaving apart for the moment the appearance of Fe(II)-oxalate and jarosite in the *Chancery MS*, the features we found in all studied samples are quadrupole doublets of  $\text{Fe}^{3+}$  species with isomer shifts of about  $0.3\text{ mm/s}$  and quadrupole splittings of about  $0.8\text{ mm/s}$  at RT. Part of this ferric iron splits magnetically at  $4.2\text{ K}$ , probably because of slow and intermediate paramagnetic relaxations, which occur typically for isolated ferric ions, for which spin-spin relaxations tend to be slow at low temperatures [37]. It is improbable that these magnetic hyperfine patterns are due to small magnetically ordered oxidic clusters similar to ferrihydrite, because these exhibit typical magnetic hyperfine splittings with broad lines and mean hyperfine fields around  $50\text{ T}$  at  $4.2\text{ K}$  [38]. An even partial assignment of the  $\text{Fe}^{3+}$  species to crystalline Fe(III)-gallate described by Wunderlich [39] can be ruled out because this compound can be prepared only at pH values above 5 and shows completely different Mössbauer parameters, particularly when it is magnetically ordered at  $4.2\text{ K}$  [40, 41]. On the basis of the quadrupole splitting at RT and the magnetic hyperfine pattern at  $4.2\text{ K}$ , one can also rule out an assignment to the second modification of Fe(III) gallate, which probably exists only as nanoparticles or may even be amorphous [42], the Fe(III) gallate(2) of [40, 41].

For an alternative assignment of this  $\text{Fe}^{3+}$  site it is worth noting that a paper impregnated with a freshly prepared Fe(II)-sulfate solution after drying shows an  $\text{Fe}^{3+}$  site with a QS value of  $0.74\text{ mm/s}$  [41] and that papers impregnated with various ink preparations show a similar site

[41]. Iron gallate or tannin complexes seem to be of minor importance for the chemical nature of iron on the papers [41]. The Mössbauer studies [41] rather suggest that iron complexes with phenols of whatever kind form only in rather small quantities in inks, while most of the reactants remain unreacted, whatever recipe is used for the ink preparation. Instead, it is apparently the free ferrous iron in the acidic ink solution that reacts with the cellulose of the paper to form ferric species with QS values of about 0.8 mm/s. The exact nature of these species cannot be determined from the Mössbauer data. The iron may be attached to the cellulose fibers. The reaction of the ferrous iron of the sulfate with the cellulose must go along with an oxidation, but in freshly impregnated dried papers, part of the iron is still  $\text{Fe}^{2+}$  [41]. Of this we see at best very little in the *Latin MS* and the cookbook, probably because the initially ferrous species oxidize in the course of time. It is worth noting that the QS values of all our samples (0.75 - 0.85 mm/s) are close to the QS values of iron-saccharose or iron-maltose complexes [43], as well as iron-humic acid or iron-polysaccharide composites [44, 45]. However, In contrast to our samples, however, these composites show the typical magnetic hyperfine splitting of ferrihydrite [44, 45].

The appearance of Fe(II)-oxalate in the Mössbauer spectra of the *Chancery MS* may appear surprising, but it does not seem to be really rare. Apart from the three documents studied in this work, there were two ancient documents studied by Danon et al. [14, 15], and three more from the National Library of Poland by Wagner et al. [16], who did not make measurements at 4.2 K. In the RT spectra of one of their three studied documents, Wagner et al. observe a prominent quadrupole doublet with the isomer shift and quadrupole splitting of ferrous oxalate, though they do not explicitly mention the presence of this compound. Thus, four out of the eight historical documents studied so far by Mössbauer spectroscopy contain ferrous oxalate.

The formation of the Fe-oxalate must be related with aging or degradation processes because it does not appear within days after ink was freshly written on paper [41]. Oxalic acid is one of the degradation products of cellulose under conditions of natural aging [46]. Together with the presence of ferrous iron, the formation of the insoluble iron(II) oxalate is quite probable. The formation of ferrous oxalate during the artificial ageing of paper impregnated with model inks has been observed by Arčon et al. [47], who studied papers impregnated with model iron gall inks by XANES and Mössbauer spectroscopy at RT. A paper aged at 80 °C and 65%

relative humidity for 7 days at a rather low pH value shows the typical quadrupole doublet of ferrous oxalate in its RT Mössbauer spectrum.

It is also possible that polyphenol complexes of the inks decompose to Fe(II)-oxalate with iron from the iron sulfate. For example, a ferrous component found as a byproduct in the synthesis Fe(III)-gallate(2) from ferrous sulfate and gallic acid at about 100 °C [40] is clearly ferrous oxalate. The exact conditions under which ferrous oxalate forms in old documents still need clarification, but prolonged storage in a warm and moist environment may be favorable for its formation.

The Fe(II)-oxalate is absent in the *Latin MS* and in the cookbook. This could be an indication for less severe paper modification, perhaps due to the low acidity of these two documents indicated by pH values of 4.7 and even higher (Table 1). Ferrer and Sistach [33, 34], however, found Fe(II)-oxalate in documents showing pH values of 4.7, 5.5 – 5.8 and even above 6. It is worth mentioning that Ferrer and Sistach [34] show an IR spectrum of a Spanish document from 1327 with a pH of 5.8 and no signs of ink corrosion, but the presence of the oxalate. However, one can clearly see in this spectrum that essential peaks of the oxalates overlap with those of the cellulose, which renders the detection of the Fe(II)-oxalate at least in this case rather difficult. The origin of this discrepancy is not clear. However, it would be very surprising if a Fe<sup>2+</sup> compound could exist at a pH above 5 for a long time, because high pH values favor the oxidation to a Fe<sup>3+</sup> state.

In the *Chancery MS* one also observes the presence of jarosite. Its presence is a clear evidence for a severe excess of Fe-sulfate as shown in the solid samples of unbalanced and aged model inks [48]. The presence of jarosite is an additional confirmation of the low pH, because it exists only in the pH range up to 4 [49].

### *Papers without ink*

The papers of the manuscripts studied in this work always contain about a factor of ten less iron than the papers with applied ink. The absolute iron contents are between 0.2 and 1 mg of Fe per gram of paper (Table 1). Iron contents of 0.1 to 1 mg/g are not uncommon in old papers [50]. The iron is found to be mainly trivalent, with at best minor traces of ferrous iron in the papers of the *Chancery MS* and the *Latin MS*. In a recent Mössbauer study of some

papers without ink Dzinavatonga et al. [18] came to a similar conclusion, but they do not give absolute values for the iron contents of their papers. The presence of iron in old papers can be due to the process of production, arising perhaps from contamination of the water used in paper production, from wear of iron machinery used in making the paper pulp from rags, or from the use of additives [51]. In the paper of the *Latin MS* there is a minor fraction of hematite that already splits magnetically at RT. At 4.2 K the Mössbauer spectrum of this paper exhibits another magnetically split component that may be attributed to fine particle goethite according to its Mössbauer parameters. Both compounds may stem from the water used in paper-making or from oxidation of metallic particles from the iron machinery used in paper production.

## **Conclusions**

In previous Mössbauer studies of papers impregnated with inks prepared by various recipes from ferrous sulfate and gallic acid, tannic acid or pyrogallol, there were always found mainly two components [40], a ferric one with a quadrupole splitting of about 0.8 mm/s and a ferrous one with a quadrupole splitting of about 2.4 mm/s at room temperature. It is improbable that these species represent specific iron complexes with the phenolic constituents of the inks, particularly since the same contributions occur in paper impregnated with iron sulfate solution only [40]. This suggests that the state of the iron even on freshly written manuscripts is mainly the result of the reaction of the cellulose of the paper and the unreacted iron sulfate of the ink. The concentration of complexes of iron with phenolic ligands is, at least in most cases, too low to be seen in the Mössbauer spectra [40]. In the course of time, and depending on the conditions of storage, iron oxalate or iron oxy-hydroxides may form from the iron compounds formed initially with the cellulose of the paper. The ultimate question about the nature of the black substance of ink on written manuscripts still seems to be unresolved, but the black species seem to be too rare to be seen in the Mössbauer spectra of papers on which ferrogalllic ink was written.

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## **Declarations**

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Table 1: Total areas of the Mössbauer spectra of the studied specimens. The iron contents were estimated from the intensities of the Mössbauer spectra as described in the text. The smaller values for the iron contents obtained from the RT spectra compared to those from the 4.2 K spectra are attributed to the decrease of the Lamb-Mössbauer factor with increasing temperature. In the last column the surface pH values of spots with ink and, for the papers only, of spots without ink are given.

Document	Absorber thickness mg/cm <sup>2</sup>	Total area at RT	Iron content mg/g	Total area at 4.2 K	Iron content mg/g	Surface pH
Chancery MS total	545	0.038	3.6	0.112	6.0	4,2 – 3.9
Chancery MS paper only	240	0.0031	0.44	0.0029	0.50	4.8
Latin MS paper with ink	219	0.037	8.8	0.11	21	4.8
Latin MS paper only	386	0.0081	1,1	0.012	1.2	5.3
Cookbook total 53 pages	360	0.014	2.0	-----	-----	---
Cookbook total 121 layers	825	0.016	1.0	0.037	1.7	4.9
Cookbook paper only 88 layers	600	0.0017	0.15	0.0011	0.07	5.7

Table 2: Mössbauer parameters obtained at room temperature and 4.2 K for the studied historical documents.

Material and assignment	Room temperature spectrum					4.2 K spectrum					
	IS [mm/s]	QS [mm/s]	B [T]	W [mm/s]	A [%]	IS [mm/s]	QS [mm/s]	B [T]	W [mm/s]	A [%]	
<i>Chancery MSpart with writing</i>											
Iron oxalate	1.09(1)	1.73(1)	---	0.28(1)	42(2)	1.08(1)	-1.96(4)	15.3(1)	0.57(1)	42(1)	
Hydronium jarosite	0.27(1)	1.24(1)	---	0.26(1)	17(2)	0.26(1)	-0.18(1)	47.8(2)	0.82(2)	22(1)	
Ferric iron doublet	0.27(1)	0.84(2)	---	0.67(2)	41(2)	0.33(2)	0.79(2)	---	0.97(7)	23(1)	
Ferric iron sextet						0.28(2)	0.05(3)	53.8(2)	0.58(4)	5(1)	
Ferrous iron doublet						1.15	2.75(3)	---	0.69(4)	8(1)	
<i>Chancery MS paper without ink</i>											
Ferric iron doublet 1	0.14(2)	0.55(4)	---	0.51(6)	51(7)	0.25(2)	0.82(3)	---	0,57(4)	50(3)	
Ferric iron doublet 2	0.24(2)	1.08(3)	---	0.38(4)	35(7)						
Ferric iron goethite						0.26	-0.22(8)	49.1	0.25*	41(3)	

Ferrous iron doublet	1.0	1.87(12)	---	0.75	14(3)	0.94(13)	3.6(3)	---	0.75	9(2)	
<i>Latin MS</i> letters with little paper											
Ferric iron	0.28(1)	0.79(1)	---	0.51(1)	100	0.28(1)	0.81(1)	---	0.61(1)	59(1)	
Ferric iron						0.29(1)	0.10(1)	52.1(5)	0.25*	6(1)	
Ferric iron						0.26	0.0	26(1)	0.25*	34(3)	
Ferrous iron						1.16	2.60	---	0.25*	1.1(5)	
<i>Latin MS</i> paper without ink											
Ferric iron doublet	0.22(2)	0.77(3)	----	0.64(3)	66(2)	0.27(1)	0.77(1)	---	0.72(2)	52(2)	
Hematite	0.25(2)	-0.25(4)	50.6(2)	0.54(8)	20(2)	0.26	-0.11(3)	53.3(2)	0.47(8)	15(5)	
Ferric iron (goethite)						0.26(1)	-0.18(3)	49.7(5)	0.25*	23(5)	
Ferrous iron	1.14(9)	2.52(20)	---	0.77(12)	14(2)	0.98(3)	2.85(6)	---	0.50	10(2)	
<i>Cookbook</i> pages 50 – 70											
Ferric iron	0.26(1)	0.75(1)	---	0.49(1)	100(1)	Not measured					
<i>Cookbook</i> single page cut into pieces											
Ferric iron	0.27	0.77	---	0.45(1)	100	0.28(1)	0.80(1)	---	0.56(1)	34(1)	
Ferric iron (lepidocrocite)						0.25(1)	-0.16(1)	45.0(1)	0.25	29(1)	
Ferric iron						0.26	0	52	0.25*	4(1)	
Ferric iron						0.26	0	32(1)	0.25*	32(2)	
Ferrous iron						1.01(3)	2.87(6)	---		1(1)	
<i>Cookbook</i> paper only											
Ferric iron	0.12(3)	0.70(3)	---	0.63(4)	100	0.22(3)	0.88(5)		0.42(7)	52(6)	
Ferric iron						0.26	0.21(1)	51.0(6)	0.25*	48(6)	

<i>Iron oxalate</i>											
Ferrous iron	1.09(1)	1.74(1)	---	0.25(1)	100	1.09(1)	-1.94(1)	14.9(1)	0.27(1)	100	
<i>Hydronium Jarosite</i>											
Ferric iron	0.27(1)	1.25(1)	---	0.29(1)	89(1)	0.24(1)	-0.13(1)	48.5(2)	0.38(2)	78(1)	
Ferrous iron	1.17(3)	2.27(3)	---	0.55(5)	11(1)	1.14(1)	3.14(2)	---	0.25	22(1)	

IS is the isomer shift relative to the  $^{57}\text{Co}:\text{Rh}$  source having the same temperature as the absorber.  $QS = eQV_{zz}/2 \cdot (1 + \eta^2/3)^{1/2}$  is the electric quadrupole interaction, B is the magnetic hyperfine field at the iron nuclei, W is the full width at half maximum of the Mössbauer lines and A is the relative area of the individual components in the Mössbauer spectrum. Values in parentheses are the last digit errors. When no error is given, the value was fixed during the fit. Components that cannot be identified with specific iron compounds are designated merely as ferric or ferrous iron. In some cases, magnetically split components were fitted with a Gaussian distribution of hyperfine fields. This is indicated by an asterisk behind the value of the Lorentzian line-width used for the distribution. More details of this are given in the text.

#### Figure captions

##### Fig. 1

Photographs of the two fragments from the Granada Library, called the *Chancery MS* (top) and the *Latin MS* (bottom).

##### Fig. 2

Photographs of the cooking book of the Widenplazerin from the year 1783: two randomly chosen pages (top) and the front page (bottom).

##### Fig. 3

Room temperature (top) and 4.2 K (bottom) Mössbauer spectra of the *Chancery MS* (left) and its rim without ink (right). In all four spectra data points are shown as black dots; the black

lines are the fits of the overall spectra. The individual spectral components of the part with writing (left) are given as colored lines: the pink and the olive lines are due to  $\text{Fe}^{3+}$  quadrupole doublets of which the latter one with the larger  $\Delta Q$  can be assigned to hydronium jarosite; the orange line is due to a  $\text{Fe}^{2+}$  quadrupole doublet assigned to Fe(II)-oxalate. In the low temperature spectrum the olive and the orange Fe doublets further split into the typical magnetic HFI sextet of the jarosite and the octet of the Fe(II)-oxalate, respectively. The second  $\text{Fe}^{3+}$  doublet remains unchanged (pink line). Two new features of minor contribution appear, the first is a magnetic HF (blue line) due to a  $\text{Fe}^{3+}$  site with slow paramagnetic relaxation and the dark cyan line can be assigned to a  $\text{Fe}^{2+}$  quadrupole doublet. The room temperature Mössbauer spectrum of the rim shows two components: a  $\text{Fe}^{3+}$  doublet (red) and a  $\text{Fe}^{2+}$  doublet (green) with an unusually small quadrupole splitting; the corresponding 4.2 K spectrum shows again the  $\text{Fe}^{3+}$  doublet (red) and a sextet due to magnetic hyperfine splitting (blue).

Fig. 4

Room temperature (top) and 4.2 K (bottom) Mössbauer spectra of the cut out calligraphic letters of the *Latin MS* (left) and the paper without letters (right). In the spectra of both samples the data points are shown as black dots; the black lines are the fits of the overall spectra. The individual spectral components are given as colored lines: the red lines are due to  $\text{Fe}^{3+}$  quadrupole doublets; the violet line in the 4.2 K spectrum of the calligraphic letters and the dark cyan lines in both spectra of the rim are due to  $\text{Fe}^{2+}$  quadrupole doublets with different  $\Delta Q$  values. The bright blue lines in the low temperature spectrum of the calligraphic letters originate from  $\text{Fe}^{3+}$  sites exhibiting slow paramagnetic relaxations. In the room temperature as well as in the 4.2 K spectrum of the rim there is a well-pronounced  $\text{Fe}^{3+}$  sextet originating from magnetic hyperfine splitting.

Fig. 5

Room temperature (top) and 4.2 K (bottom) Mössbauer spectra of a written (left) and an empty page (right) of the cooking book. In all the spectra the data points are shown as black dots and the black lines are the fits of the overall spectra. The individual spectral components are given as colored lines. In all four spectra there is a  $\text{Fe}^{3+}$  quadrupole doublet (red lines) with roughly

the same quadrupole splitting. In the low temperature spectra of the written as well as in the empty page there are magnetic sextets (dark blue): two in the written page and one in the empty page. In the 4.2 K spectrum of the written page there is a very broad feature (bright blue) due to  $\text{Fe}^{3+}$  showing slow paramagnetic relaxation.

Fig. 6

Room temperature (left) and 4.2 K (right) Mössbauer spectra of Fe(II)-oxalate (top) and hydronium jarosite (bottom).

Figure 7

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra of the *Chancery MS* and the *Latin MS*. Both show the dominance of the cellulose spectra.

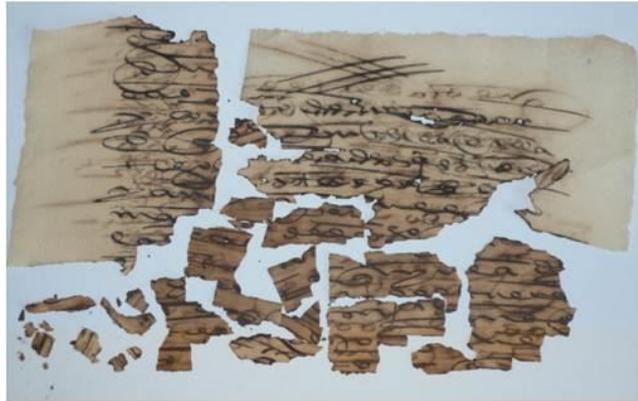


Fig. 1

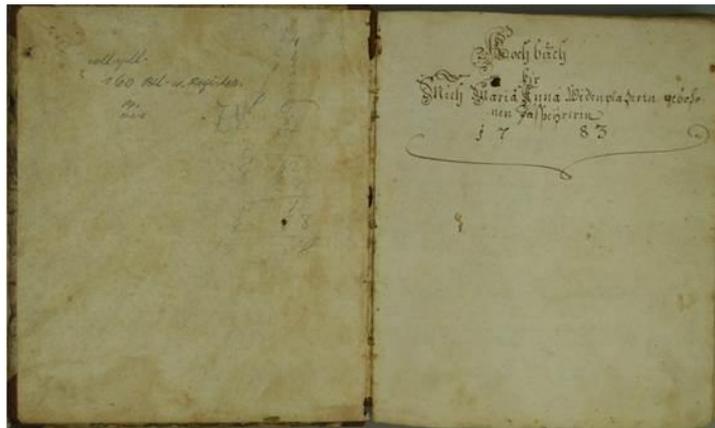
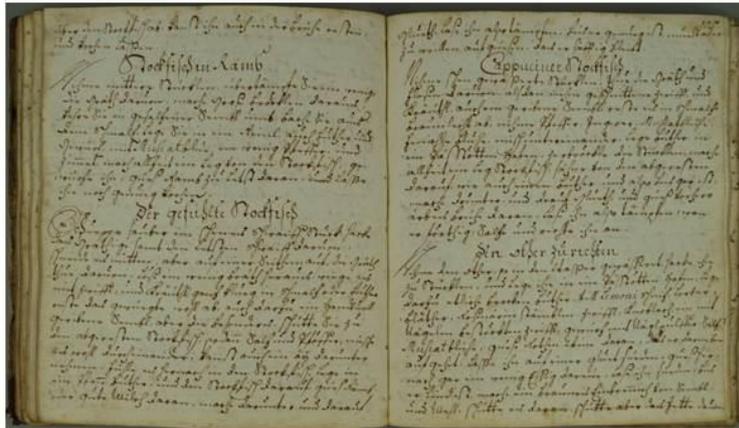


Fig. 2



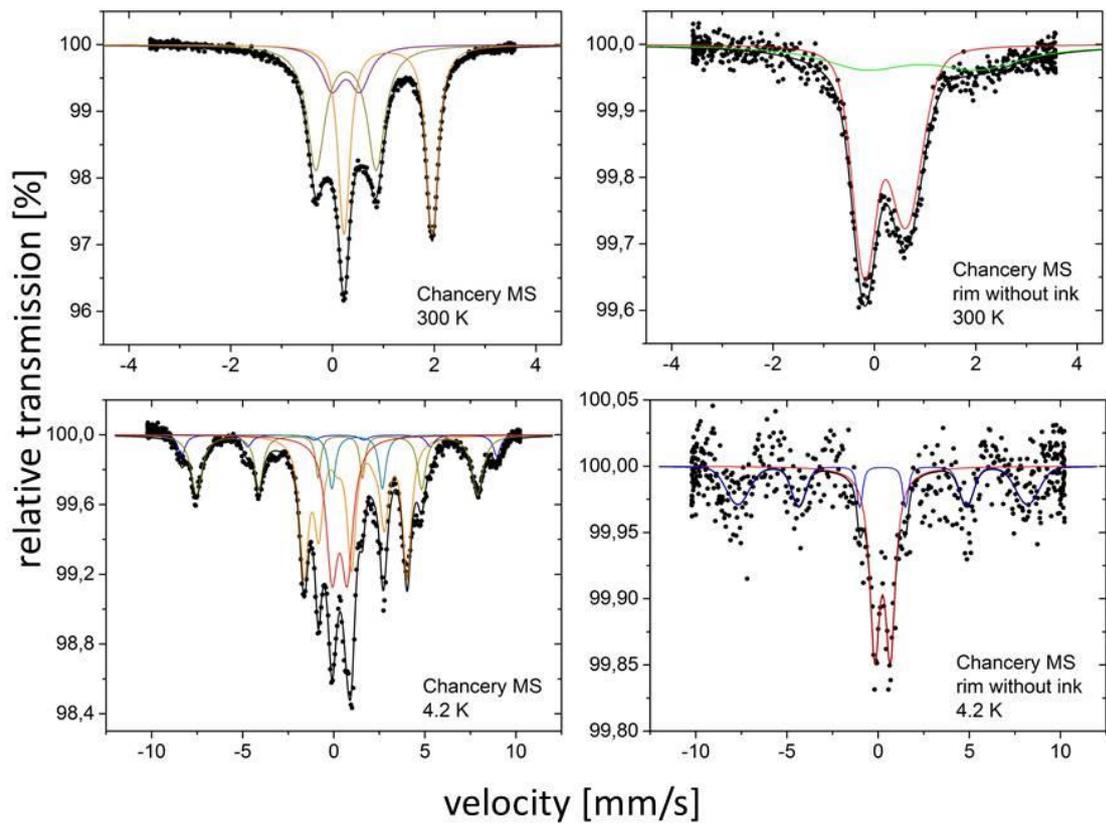


Fig. 3

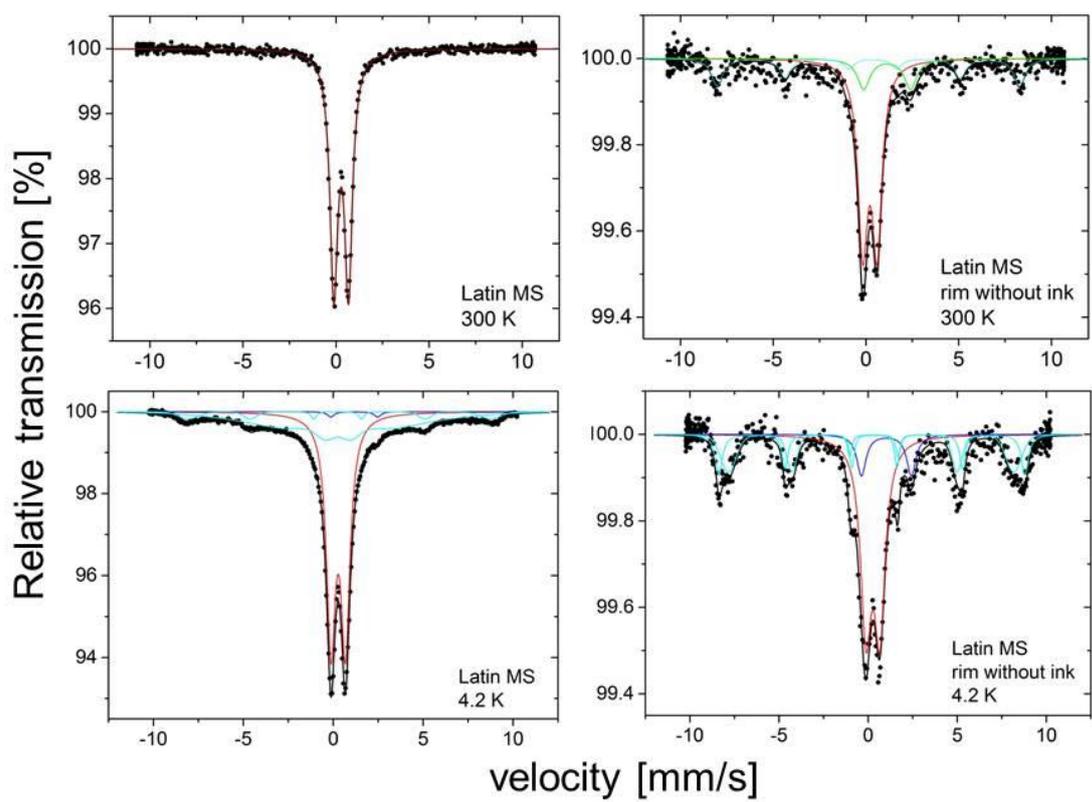


Fig. 4

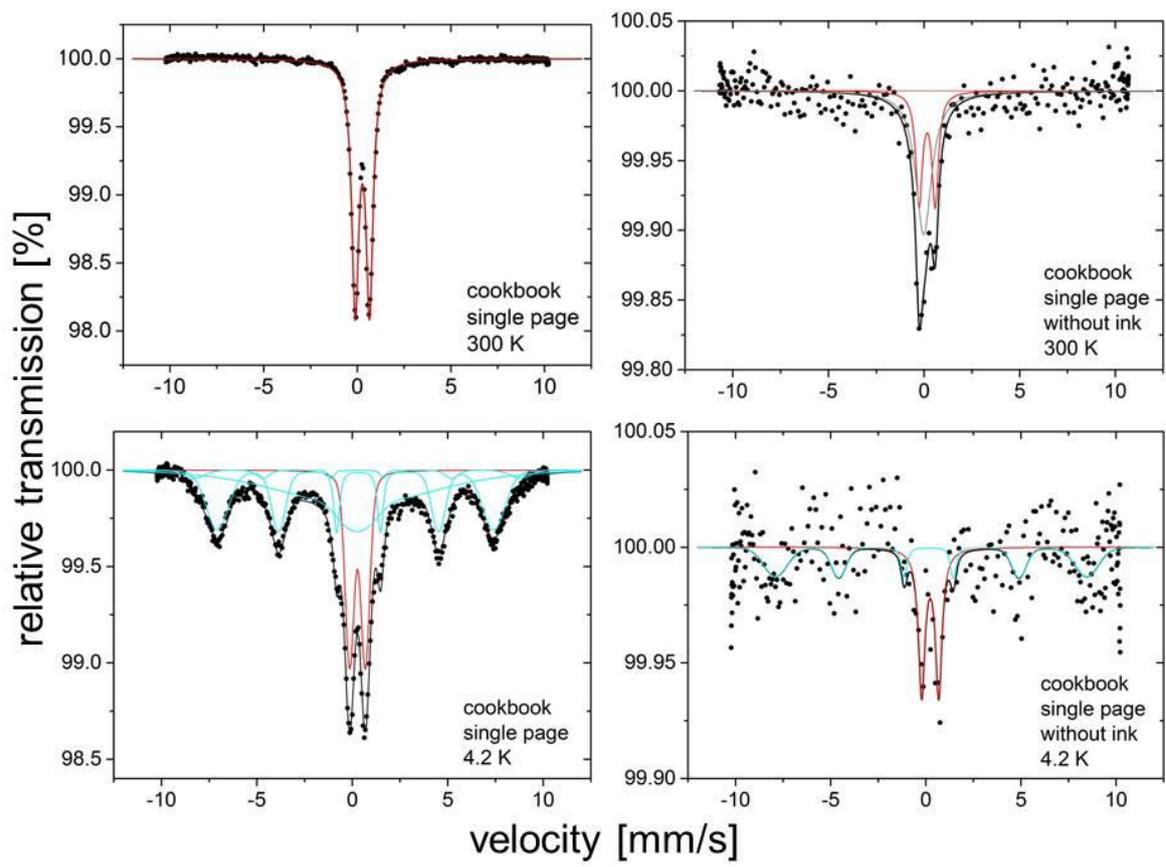


Fig. 5

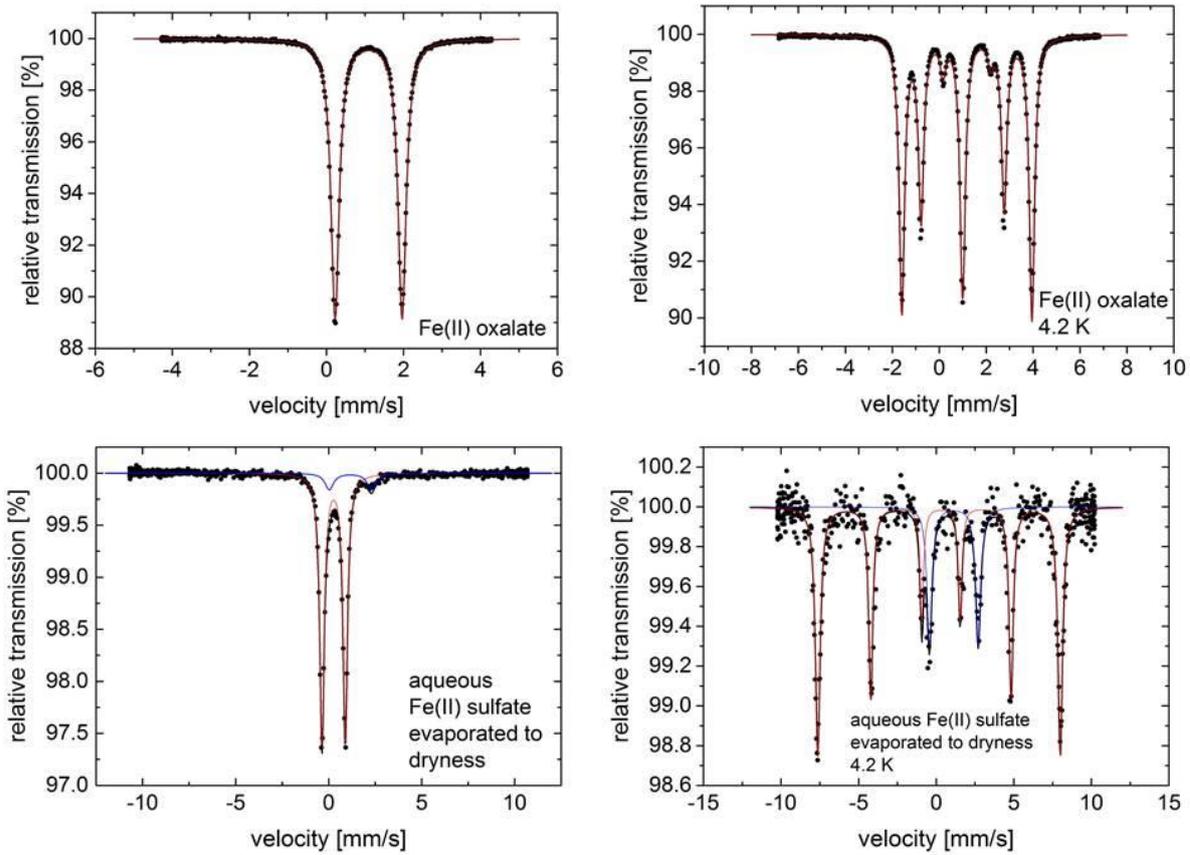


Fig. 6

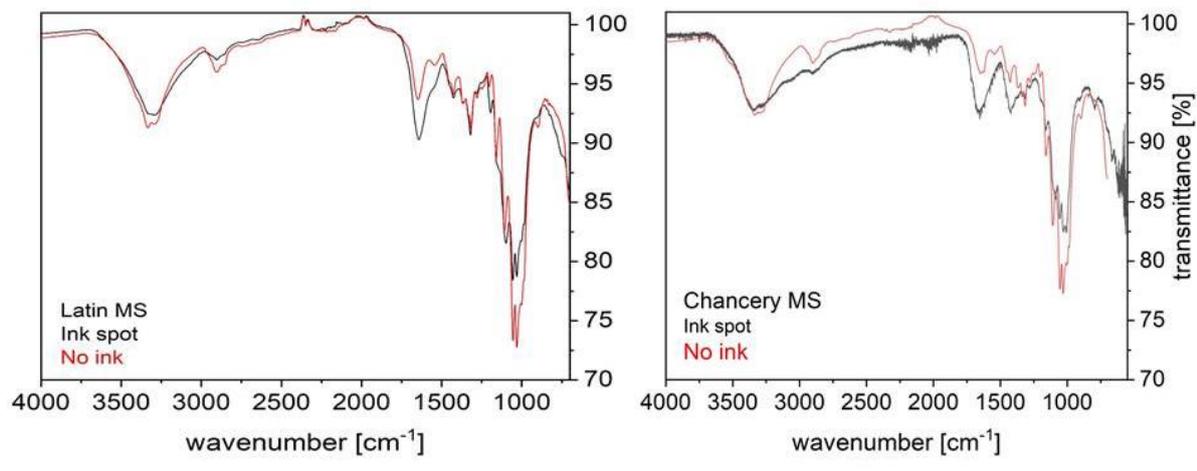
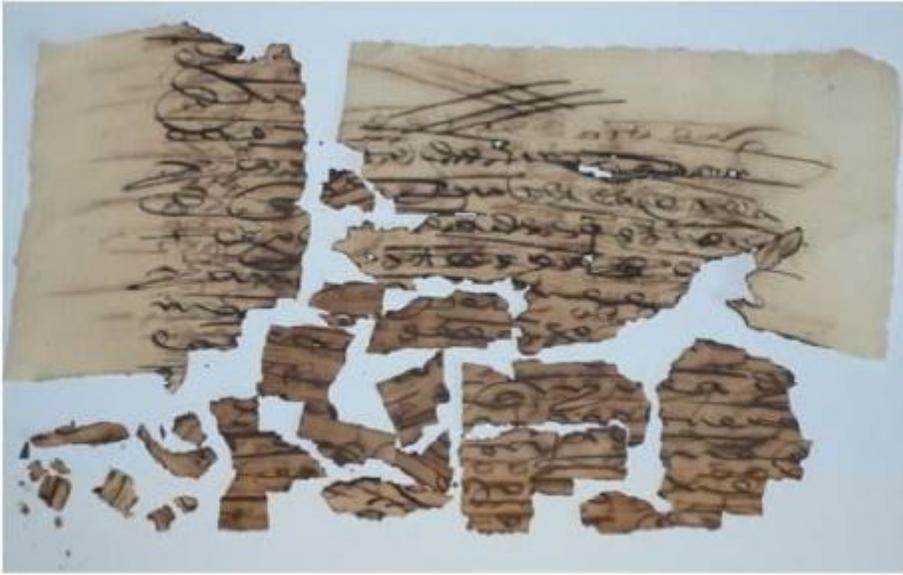


Fig. 7

# Figures



**Figure 1**

Photographs of the two fragments from the Granada Library, called the Chancery MS (top) and the Latin MS (bottom).

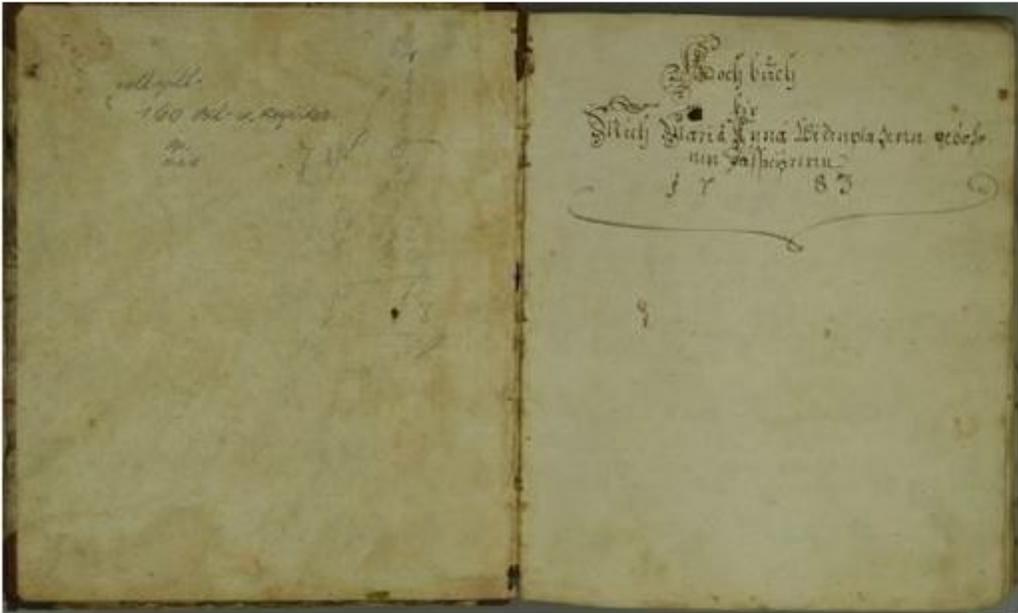
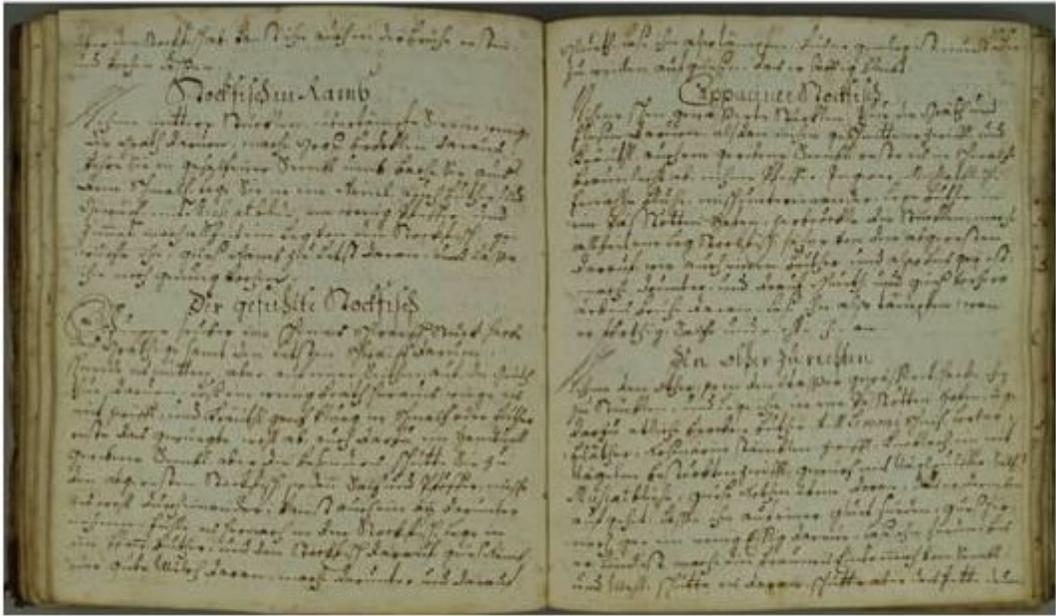
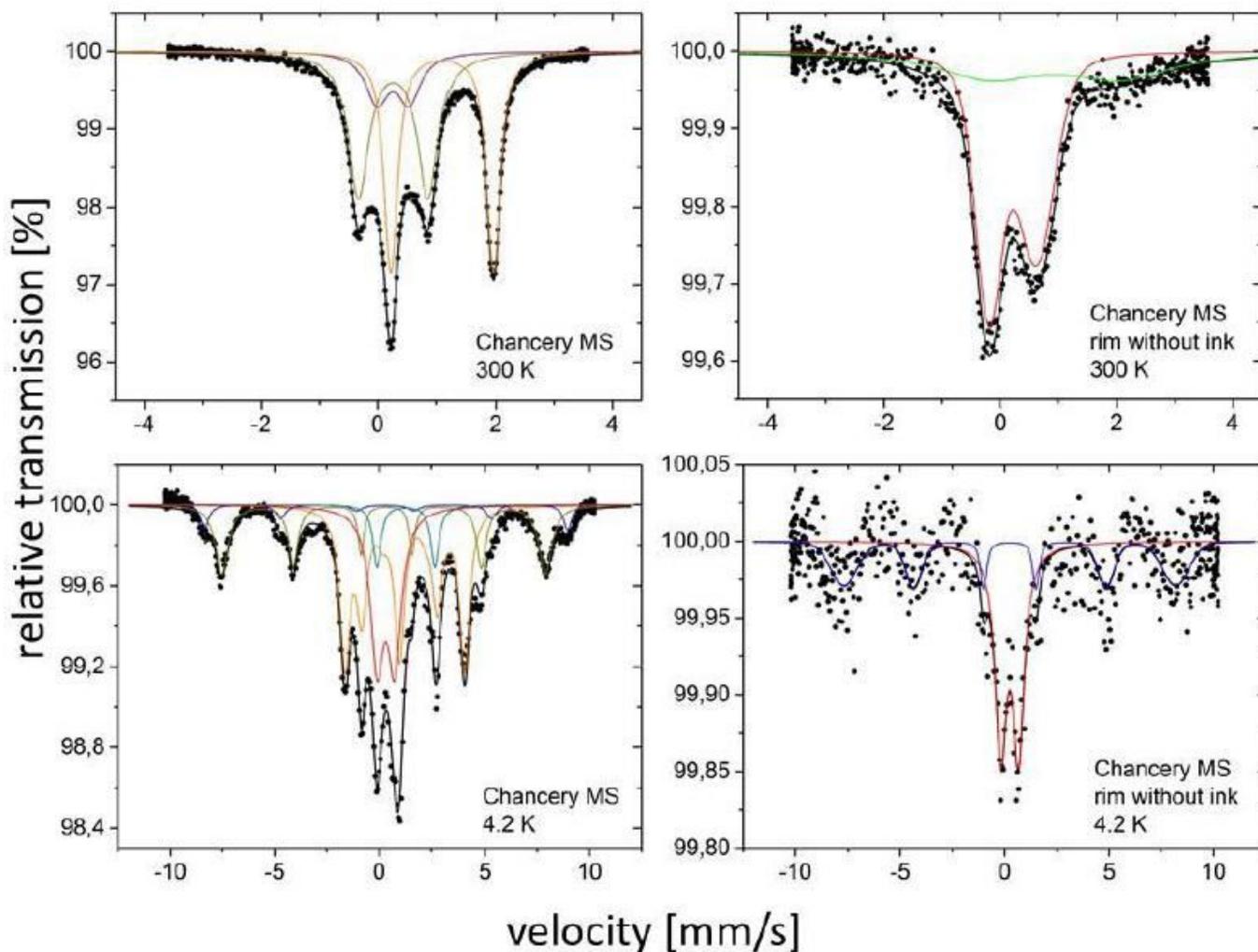


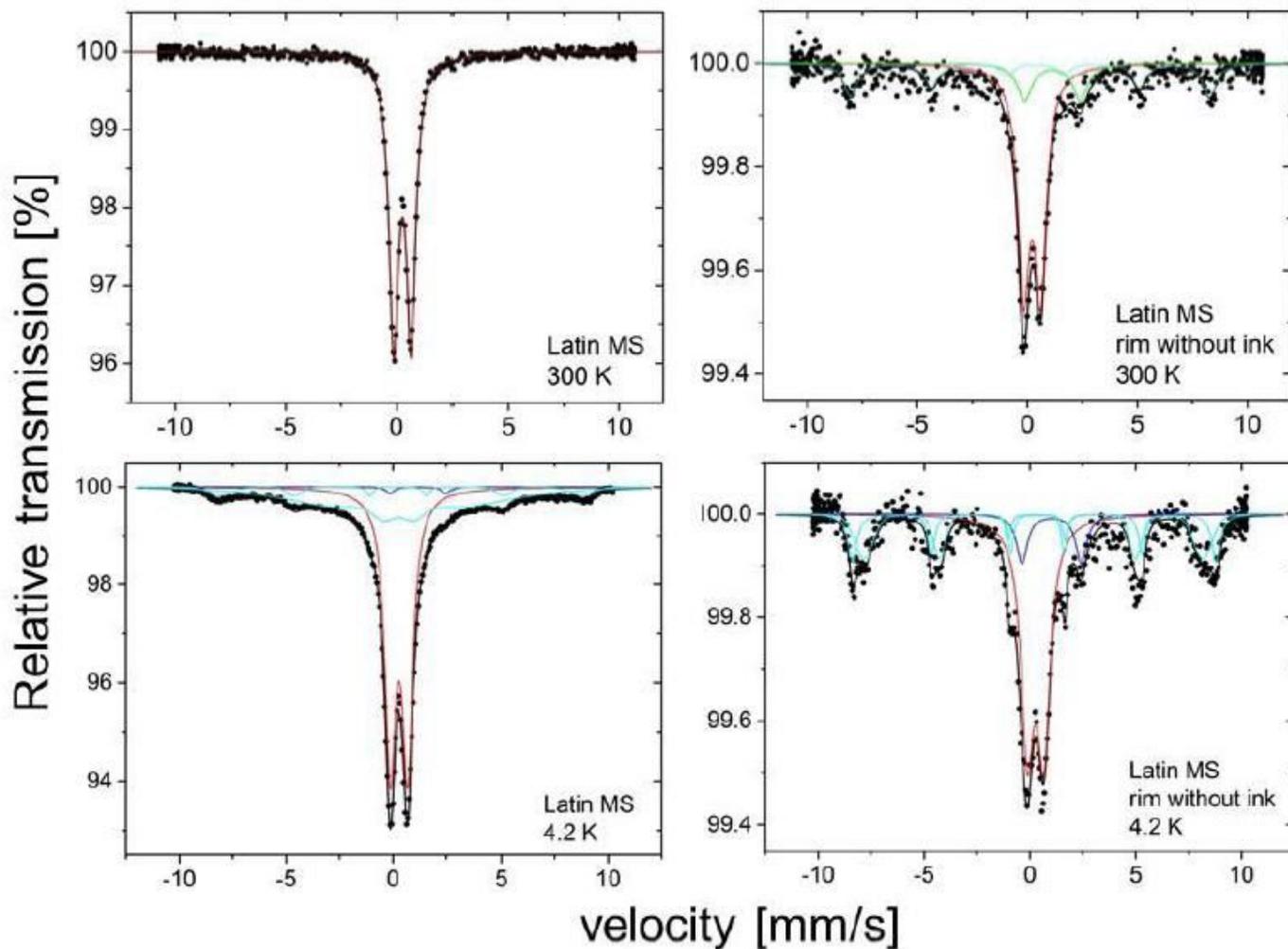
Figure 2

Photographs of the cooking book of the Widenplazerin from the year 1783: two randomly chosen pages (top) and the front page (bottom).



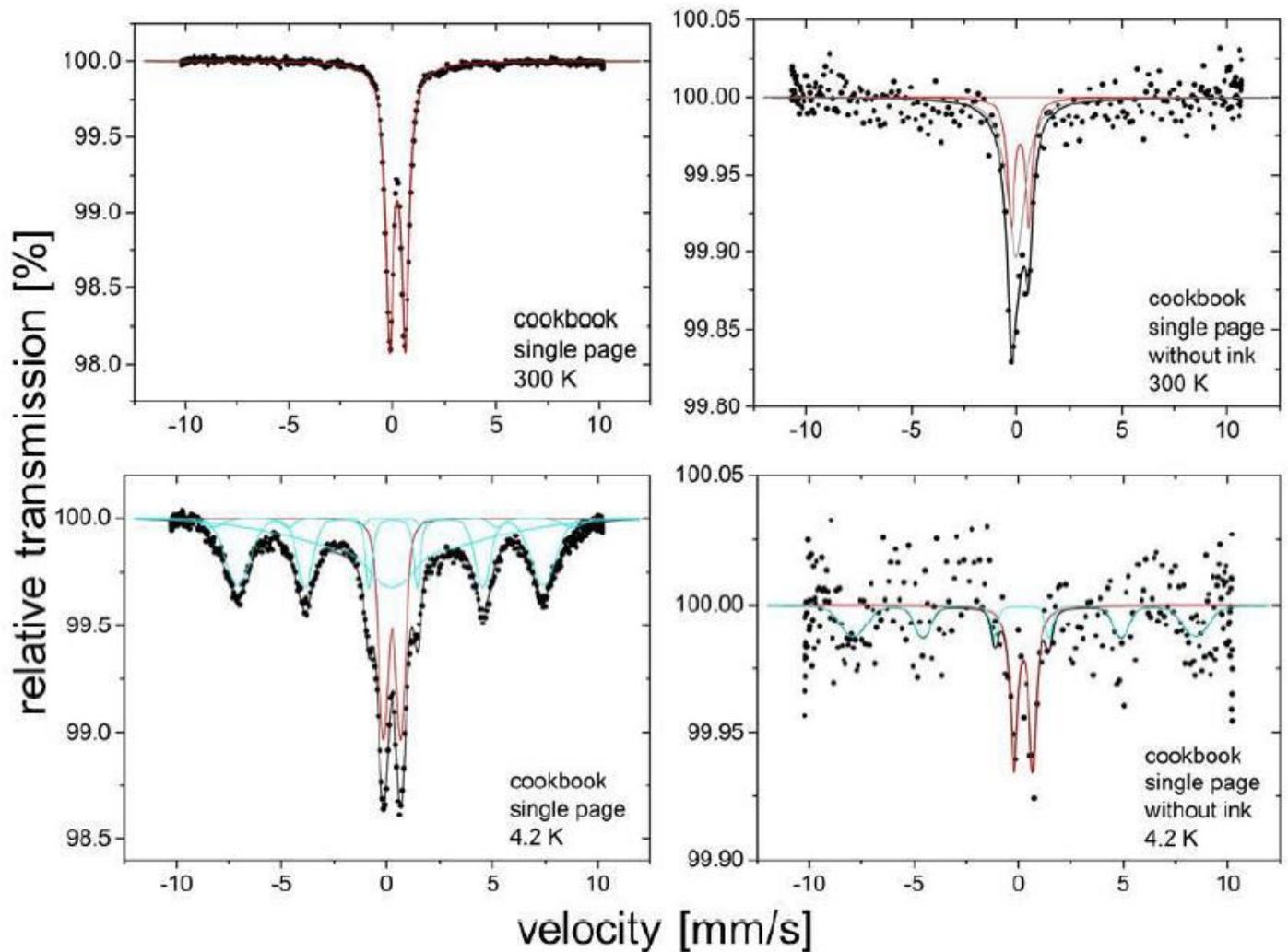
**Figure 3**

Room temperature (top) and 4.2 K (bottom) Mössbauer spectra of the Chancery MS (left) and its rim without ink (right). In all four spectra data points are shown as black dots; the black lines are the fits of the overall spectra. The individual spectral components of the part with writing (left) are given as colored lines: the pink and the olive lines are due to  $\text{Fe}^{3+}$  quadrupole doublets of which the latter one with the larger  $\Delta Q$  can be assigned to hydronium jarosite; the orange line is due to a  $\text{Fe}^{2+}$  quadrupole doublet assigned to  $\text{Fe(II)-oxalate}$ . In the low temperature spectrum the olive and the orange  $\text{Fe}$  doublets further split into the typical magnetic HFI sextet of the jarosite and the octet of the  $\text{Fe(II)-oxalate}$ , respectively. The second  $\text{Fe}^{3+}$  doublet remains unchanged (pink line). Two new features of minor contribution appear, the first is a magnetic HF (blue line) due to a  $\text{Fe}^{3+}$  site with slow paramagnetic relaxation and the dark cyan line can be assigned to a  $\text{Fe}^{2+}$  quadrupole doublet. The room temperature Mössbauer spectrum of the rim shows two components: a  $\text{Fe}^{3+}$  doublet (red) and a  $\text{Fe}^{2+}$  doublet (green) with an unusually small quadrupole splitting; the corresponding 4.2 K spectrum shows again the  $\text{Fe}^{3+}$  doublet (red) and a sextet due to magnetic hyperfine splitting (blue). Fig. 4



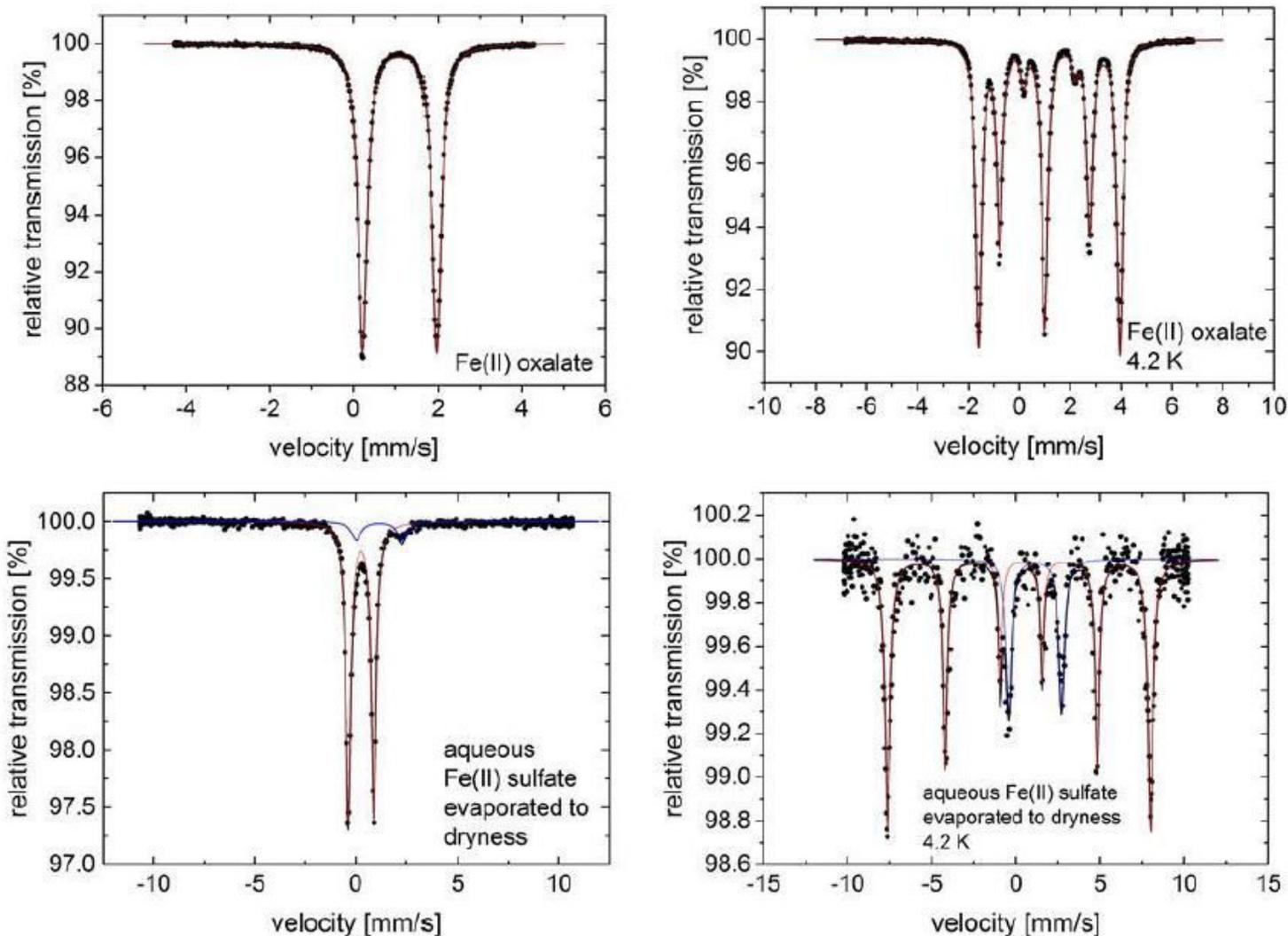
**Figure 4**

Room temperature (top) and 4.2 K (bottom) Mössbauer spectra of the cut out calligraphic letters of the Latin MS (left) and the paper without letters (right). In the spectra of both samples the data points are shown as black dots; the black lines are the fits of the overall spectra. The individual spectral components are given as colored lines: the red lines are due to Fe<sup>3+</sup> quadrupole doublets; the violet line in the 4.2 K spectrum of the calligraphic letters and the dark cyan lines in both spectra of the rim are due to Fe<sup>2+</sup> quadrupole doublets with different  $\Delta Q$  values. The bright blue lines in the low temperature spectrum of the calligraphic letters originate from Fe<sup>3+</sup> sites exhibiting slow paramagnetic relaxations. In the room temperature as well as in the 4.2 K spectrum of the rim there is a well-pronounced Fe<sup>3+</sup> sextet originating from magnetic hyperfine splitting.



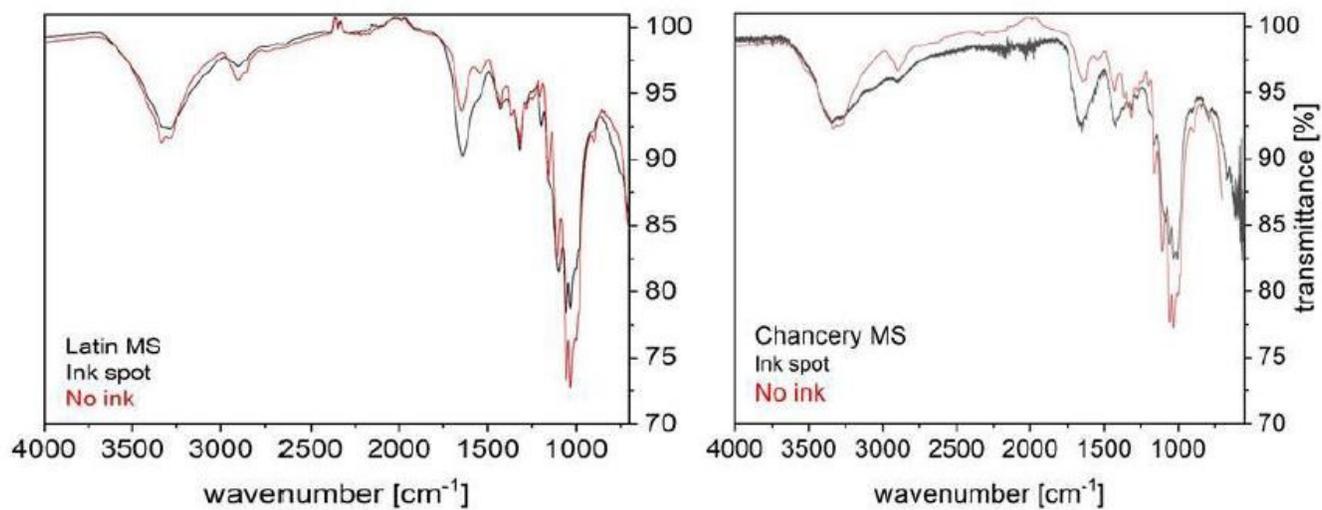
**Figure 5**

Room temperature (top) and 4.2 K (bottom) Mössbauer spectra of a written (left) and an empty page (right) of the cooking book. In all the spectra the data points are shown as black dots and the black lines are the fits of the overall spectra. The individual spectral components are given as colored lines. In all four spectra there is a  $\text{Fe}^{3+}$  quadrupole doublet (red lines) with roughly the same quadrupole splitting. In the low temperature spectra of the written as well as in the empty page there are magnetic sextets (dark blue): two in the written page and one in the empty page. In the 4.2 K spectrum of the written page there is a very broad feature (bright blue) due to  $\text{Fe}^{3+}$  showing slow paramagnetic relaxation.



**Figure 6**

Room temperature (left) and 4.2 K (right) Mössbauer spectra of Fe(II)-oxalate (top) and hydronium jarosite (bottom).



**Figure 7**

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra of the Chancery MS and the Latin MS. Both show the dominance of the cellulose spectra.