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On the Origin of the Ink of the Thanksgiving Scroll (1QHodayot[a])

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Abstract

In this study we demonstrate the possibility to identify the production area of the scrolls, coupling non-destructive quantitative analysis of trace elements to spectroscopic investigation of the inks. This approach, that allowed us to determine the Dead Sea area as origin of 1QHodayot[a], is of general validity.

Keywords

1QHodayot[a]; archaeometry; material research; carbon ink

Principle

Our approach is based on the determination of the ratio of the elements chlorine and bromine in parchment and inks, which ratio serves as a fingerprint of the water used in the production process.

Water bromine content is usually small as compared to chlorine, with typical Cl/Br ratio of 300 for seawater. But in the Dead Sea, the world largest reservoir of bromine, the content of bromine salts is extremely high and Cl/Br ratios as low as 30 have been measured in its water. In the western coastal region even fresh spring water display unusually high bromine ions concentration. Based on the results of surveys performed during the last 70 years, one can firmly place the Cl/Br ratio within the limits 30–100 [1–4, 23–25]. Since industrial exploitation of the Dead Sea is a recent activity on the time scale involved here, the current range of Cl/Br ratio can be regarded as an upper limit for that in the historical age of interest.

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Carbon inks were usually stored as dry pellets and mixed with water directly before writing [5]. Therefore, the ratio of trace elements in the inks should mirror that in the water used as solvent. This would allow us to localize the production area of the scrolls. To verify our approach we performed a series of experiments: pieces of modern parchment were inscribed with Chinese ink mixed with water from different water sources in the vicinity of the Dead Sea and analyzed for the chlorine/bromine ratio. This series of measurements has shown that the inked area displayed characteristically low values of Cl/Br ratio. In the control experiments Chinese ink was mixed with de-ionized water whereupon no chlorine or bromine could be detected in the ink layer. Thus, our approach is eligible for determining the Dead Sea region as geographic origin of the scrolls [6].

Notes on the Fragment under Study

The scroll known as 1QHodayot[a], has a relatively simple history. One of the first 7 scrolls discovered by Bedouins in Qumran Cave 1, it was among the first two scrolls acquired by Eliezer Sukenik on November 29, 1947. Sukenik reports he received the scroll as recovered by Bedouins from the jar where, allegedly, it was stored [7]. Thus, we expect it to show minimal traces from the mineral deposits of the cave rocks. James Biberkraut, who unrolled the scroll, only employed a high humidity chamber [8]. Given the relatively good preservation state of the small fragments as documented by the photos executed upon unrolling the scroll, no major restorative intervention was required. Hence, post-discovery alteration of the scroll was induced by natural ageing and storage environment.

The text has been studied intensively during the last 60 years. The composition is generally regarded to be one of the core sectarian texts in the corpus of Dead Sea scrolls, belonging to a sect which is commonly associated with the Khirbet Qumran settlement. Whereas the most ancient copy of the Hodayot (4Q428) might precede the period of settlement of Qumran, the date of the 1QH[a] manuscript coincides with the period of settlement. Therefore, despite the lack of any archeological evidence up to now, this scroll is generally believed to have been written in Qumran [9, 10].

The upper part of Fig. 1a shows a recently taken photograph of the fragment under study. The infrared image below was made in 1948 [11] upon the unrolling of the scroll and appears in the plate 58 of Sukenik's publication [7]. Intense black colour of the inscriptions, apparently unaffected by ageing, is characteristic of a carbon ink, which fact is in accord with the previous studies of the inks of the Dead Sea Scrolls [12,13]. In addition, optical microscopy has shown that extremely thin ink layers display remarkable adhesion that is similar to that of iron gall ink, invented only some centuries later.

Experimental

X-ray Fluorescence (XRF). Profile scans were carried out with the mobile energy dispersive micro-X-ray spectrometer ArtTAX© (Bruker AXS Microanalysis GmbH, formerly Röntec-GmbH, Berlin, Germany), which consists of an air-cooled low-power X-ray tube, poly-capillary X-ray optics (measuring spot size 70 µm diameter), an electro-thermally cooled Xflash detector, and a CCD camera for sample positioning. Furthermore, open helium purging in the excitation and detection paths allows for detecting of light elements ($z \geq 11$). All measurements were made using a 30 W low-power Mo tube, 50 kV, 600 µA, and with an acquisition time of 70 s (live time).

Fourier-Transform Infra Red spectroscopy (FTIR). For acquiring transmission FT-IR spectra, micro samples were placed on ZnSe windows and measured at room temperature. A 15x IR objective with an aperture of 50 µm × 50 µm was used to focus the beam on the sample. An FT-IR microscope (Hyperion 2000) equipped with a liquid nitrogen cooled MCT detector and connected to a Vertex 70 FT-IR spectrometer (Bruker GmbH, Germany) was used. A total of 512 scans were co-added per sample spectrum (wavenumber range: 4,000–700 cm^{-1}) and apodized, applying the Blackman–Harris three-term function and a zero filling factor of 2.

Scanning Electron Microscopy (SEM): FEI Quanta 200 FEG, EDX system: EDAX Genesis 4000 with Si(Li) detector, type Sapphire. The measurements were carried out at accelerating voltage of 20kV, pressure of 1.1kPa in H2O vapour, Secondary Electron (SE) mode plus Back Scattered Electrons.

Results and Discussion

The results presented here were measured on the ink spot: the thick layer of ink in that area allowed for reliable measurement of ink composition.

The electron scanning micrograph in Fig. 1b shows the parchment/ink border. The parchment surface structure, clearly visible on the left side, is completely covered by the ink layer to the right side of the micrograph. This explains the intense and uniform coloration of the text shown in the infrared picture and clearly demonstrates the unusual adhesion characteristic of this ink.

We used X-ray fluorescence methods to analyze elemental composition profiles, i.e. elemental composition as function of the coordinate, of parchment and ink. Fig. 2 shows an x-coordinate profile of the chlorine to bromine concentration ratio. The measured intensities were quantified using fundamental parameters approach and an algorithm correcting the effect of porous matrix. All of the scans have been measured along the trajectory visible in the upper part of the figure, starting from the position indicated by the marker and moving 7.7 mm rightward. We observe that the fall of Cl/Br ratio coincides exactly with the inked area. Since the writing of the text, both parchment and ink inscription have undergone the same history. Therefore, the composition differences must reflect differences between parchment and ink composition before the inscription was made, i.e.: from their fabrication. Since both parchment and ink making involve handling with water, the difference in the ratio of Cl to Br indicates that water from different sources was used in the production processes. Remembering that inks were usually stored as dry pellets and mixed with water directly before writing we conclude that the low chlorine to bromine ratio is characteristic of the water used for the ink preparation just before writing. Hence the composition indicates that writing took place in the vicinity of the Dead Sea.

It is noteworthy that the values of Cl/Br measured on parchment correspond to the higher limit for water associated with the Dead Sea area, suggesting that parchment may have been also produced in the Dead Sea area.

The concentration profiles for Ca and K are also presented. The higher concentration of potassium found within the inked area is consistent with use of potassium rich natural gums. Elevated concentration of calcium, on the other hand, is not limited to the ink layer but scattered throughout the whole surface as result of dust accumulation. Absence of calcium phosphate and the distribution of calcium point at a vegetable origin of the soot. Had bones been used for the preparation of the soot, the calcium concentration profile would certainly be higher in the inked area.

The infrared spectrum of the parchment in the vicinity of the inks is characterized by prominent amide A, B absorption bands in the region

3000-3400 cm^{-1} and amide I and amide II peaks at 1648 and 1540 cm^{-1}, respectively. The form, position and separation of the amide peaks at 1648/1540 cm^{-1} closely resemble data reported previously [14]. It is noteworthy, that bands associated with tannins were not observed in previous and the current study. Thus, the hypothesis of surface treatment with tannic agents, proposed in the sixties in the famous study of Ronald Reed [15] cannot be substantiated in this case.

Carbon ink, probably the oldest ink historically documented, consists of three basic components, soot, tree sap and water. Gum Arabic, a gum from acacia Senegal, is a known ingredient of inks, cosmetics and medicines since the antiquity [5,16]. It belonged to the trade items of the ancient Egypt—collected in forests like formations in the area corresponding today to Sudan. The high water solubility of this light-coloured gums of almost purely polysaccharide nature is probably responsible for their prevalence and dissemination throughout the world since the antiquity. Quite naturally it was expected in the inks of the Dead Sea Scrolls. The solid line in fig. 3 is the first Fourier Transform Infra-Red (FTIR) spectrum of Dead Sea Scroll ink ever reported. Its shape is similar to that of natural gum. However its many peaks are sharper, suggesting the presence of tannins and aromatic compounds. Two types of vegetable tannins can be distinguished based on their infrared spectra: condensed and hydrolysable tannins. The former are of phenolic nature and do not have carboxylic groups whereas the latter (e.g.: gallic acid) do possess such groups [17,18].

The two types of acacia growing to the north of Egypt in the Red Sea and Dead Sea regions, are known under the common names of Umbrella Thorn acacia (acacia tortilis) and Spiraled Acacia (raddiana Savi) [19,20]. They also deliver water-soluble gums that were used locally throughout the centuries as substitutes for the expensive foreign Gum Arabic. Almost black in colour, they contain high quantities of condensed tannins in addition to polysaccharides. Dotted curve corresponds to the spectrum of the sample from acacia raddiana gum. Though similar in shape, local acacia does not show the band in the region of 1750 cm^{-1} characteristic of the spectrum of hydrolysable tannins. To our astonishment the best correspondence was found when comparing the spectra of the ink from the scroll with a sample of ours prepared according to Maimonides recipe, dating from the 12th century (grey curve) [21]. Curiously enough, Maimonides recommends adding gall nuts extract to the common ingredients of the carbon black ink, without mentioning any reason. For the preparation of our sample we used commercial Gum Arabic and oak galls. The infrared spectra obtained combining tannins with natural resin seems to fit much better the experimental results from the original ink than the spectra obtained using single type of binders. Thus, the direct addition of a tannic agent to the inks cannot be excluded: Maimonides' prescription could indicate the survival of an ancient use, whose actual reason had been forgotten. In this case the tannins would chemically bind the ink to the parchment collagen [22], explaining the surprising durability of the scroll inks as compared to the usual, physisorbed, carbon-based ink.

In this discussion of the spectroscopic results we disregard the aging effect, as it should broaden the peaks rather than shift their positions.

The IR spectroscopic evidence together with the very durability of the writings supports our interpretation that tannins are present in the ink. A crucial test would now be the investigation of the ink-parchment interface from a cross section cut. But such a major destructive incision into a scroll is not justifiable at the moment.

Further study of the inks and parchments of the Dead Sea Scrolls regarding inks binder in addition to the composition would add another dimension to the atlas of inks and parchment we are currently compiling.

Conclusion

Using the fingerprint composition of the water from the Dead Sea region we could directly link the fragment, and consequently, the production of 1QHodayot[a] to the Qumran area. Furthermore, our study of the organic components present in the carbon ink of this scroll indicates that gall nuts extracts were used in the ink preparation as early as 1st century C.E.

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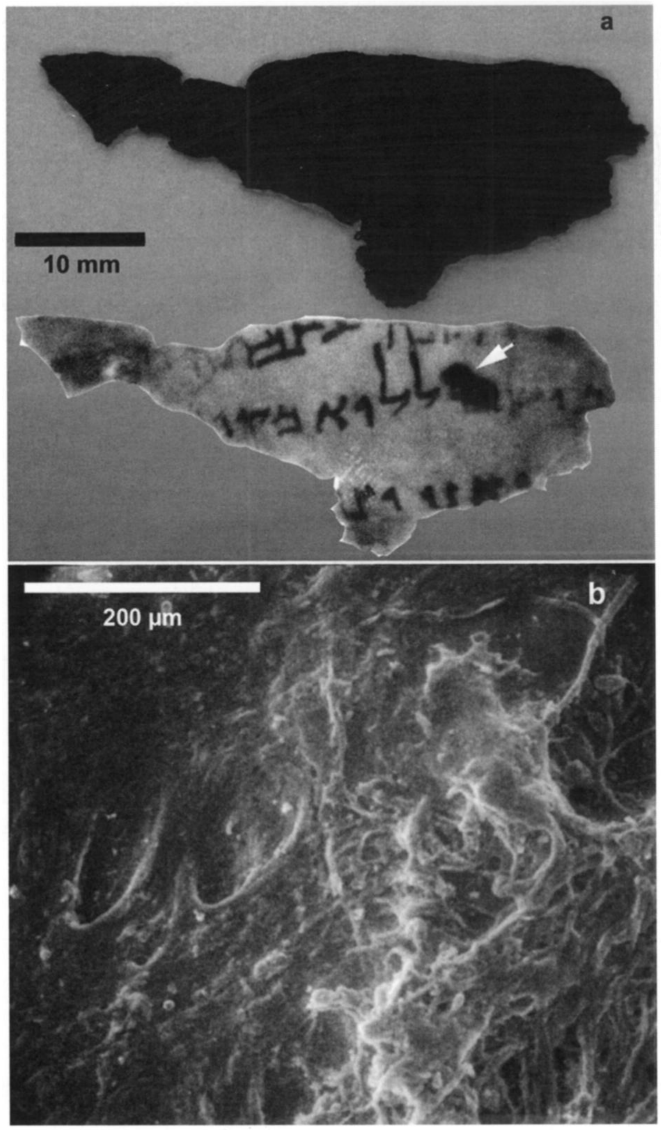

Fig. 1: Images of the fragment 52 (Sukenik fragments) from the 1QHodayot[a] scroll. In the reconstructed scroll this fragment is now placed in col. XXII 17–19 [DJD 40; plate XX]

a) recent view of the fragment (upper) and infra red photograph taken from the plate 58 in [6] (lower). White arrow indicates the spot tested.
b) Electron scanning micrograph of the parchment and ink area at the ink spot edge.

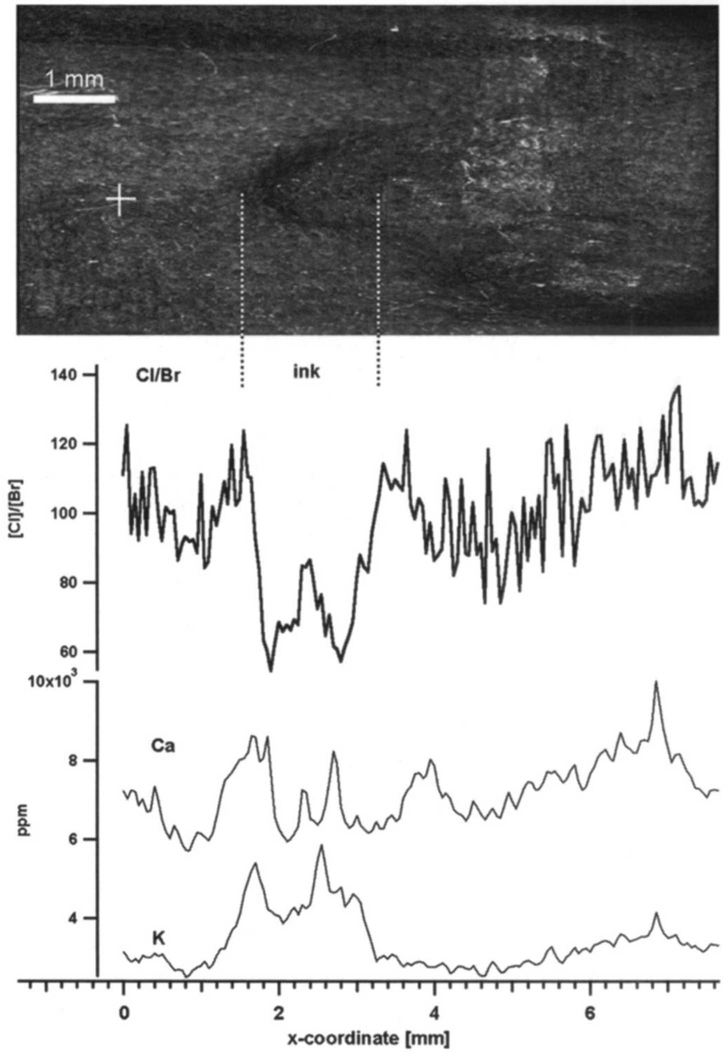

Fig. 2: x-coordinate profile of the elements and a micrograph of the spot under investigation.

top: Micrograph of the ink spot; the white cross indicates the beginning of the scan with X-ray fluorescence spectrometer.

middle: Profile of the concentration ratio of the elements Cl to Br.

bottom: Profiles of the elements Ca and K.

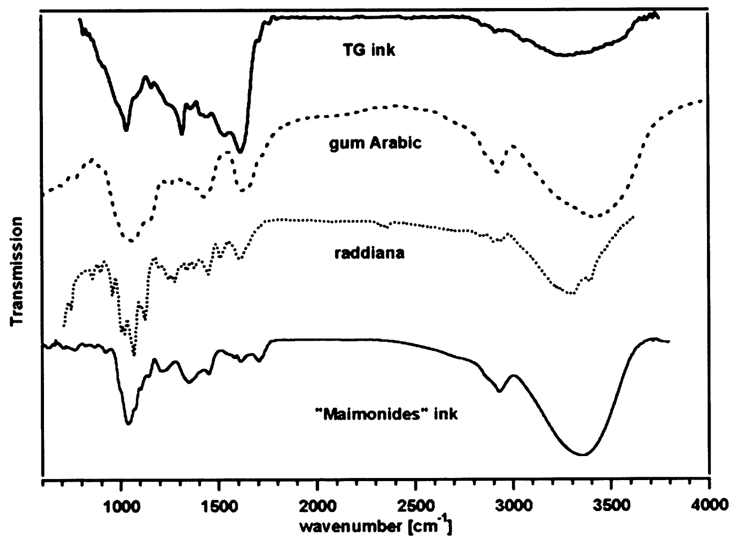

Fig. 3: FTIR spectra from top to bottom: an ink sample from the 1QH[a] scroll, a sample of gum Arabic, gum Raddiana, ink prepared according to Maimonides' recipe that contains gum Arabic and oak galls extract.