

1 April 2009

Mr. Kevin Repp
Curator of Modern European Books and Manuscripts
Beinecke Rare Book and Manuscript Library
121 Wall Street
New Haven, CT 06511

Subject: Materials Analysis of the Voynich Manuscript
Re: McCrone Associates Project MA47613

Dear Mr Repp:

We have completed our analysis of the Voynich Manuscript, which we examined and sampled at the Sterling Library conservation laboratory on 14 and 15 January 2009. This work was performed under authority of the purchase order dated 11/28/2008 from ProOmnia Film & Video Promotion GmbH.

EXAMINATION

The manuscript, a codex, is 23.5 cm high by 16.2 cm wide by about 5 cm deep and is in fair condition. Bound in vellum with vellum pages, it is approximately 240 pages long, and consists of text, which is currently undeciphered, and illustrations.

The writing is in a brownish-black ink of variable darkness. The sizes of the letters vary from page to page, but are generally consistent within a particular page. The writing appears to have been written with a quill pen.

When examined with ultraviolet radiation, the paints appear quite dark, and the writing is a deep velvety purple-black, suggesting an iron gall ink. Ultraviolet examination of Folio 1R revealed the presence of a signature, probably that of Jacobj à Tepenece. Other, undeciphered writing was seen as well. Many parts of this page exhibit a blotchiness consistent with chemical staining which, it was said, had been applied in order to enhance the writing. It may also have had the long term result of washing away some of the original writing.

SAMPLE COLLECTION

Samples of ink and paint were taken from locations recommended to us by Dr. Alfred Vendl, Institutsvorstand, Institut für Kunst und Technologie, Universität für angewandte Kunst in Vienna, Austria, and in consultation with ProOmnia representatives.

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The samples were collected using an extremely fine-pointed tungsten needle and a microscalpel. The subjects sampled and their locations are summarized in Table I.

During the sampling, photomicrographs of each of the sampled locations (with the exception of Sample 16) were made with a stereomicroscope, usually at 1X magnification with a 2.5X photo-eyepiece. The photomicrographs are included as figures in this report.

PREPARATION

A portion of each sample was mounted onto a glass microscope slide for polarized light microscopy (PLM) analysis, onto a beryllium planchet for energy dispersive X-ray spectrometry (EDS) in the scanning electron microscope (SEM), onto glass pins for micro X-ray diffraction (XRD), and onto a potassium bromide substrate for infrared spectroscopy analysis (IR) of the media.

ANALYSIS

The samples were analyzed by a combination of PLM, IR, XRD and EDS in the SEM. The results of our analyses are also summarized in Table I, and the spectra generated during the analyses are included as Figures 1B through 20F in this report.

EXAMINATION OF THE BLACK INKS

All of the ink samples were examined by PLM. All of the inks examined, text, drawing, page number, quire number and the "a" on Folio 1 Recto, had similar microscopical characteristics. The particles were consistently a brownish-black color, although there was considerable variation in the opacity (darkness) of the inks; the opacity correlates roughly with the amount of iron present in the EDS spectra. The particles are transparent, isotropic flakes with irregular or conchoidal fracture, and with refractive indices lower than 1.662. Some of the particles were adhered to the vellum substrate, in which case they also often included small particles of anisotropic calcium carbonate. Calcium carbonate is normally found on vellum and was used in its manufacture. Sample 16 also included several very dark opaque particles of more concentrated ink, and Sample 20 included a red-brown particle with characteristics consistent with burnt sienna, a common iron oxide.

Most of the ink samples are chemically quite similar to one another, based on their elemental analyses as performed by EDS in the SEM. Largely, the inks contained iron, sulfur, calcium, potassium, and carbon in major amounts, with trace amounts of copper and occasionally zinc. Iron gall inks normally contain iron, sulfur and carbon, and

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frequently potassium. Small amounts of copper and zinc are a little unusual. Sources for these elements may be as minor contaminants in the iron source, or possibly due to the use of a brass inkwell; the actual source is unknown.

X-ray diffraction provides information about the crystal phases present in a sample. In Sample 2, it identified three crystalline materials, potassium lead oxide, potassium hydrogen phosphate and syngenite, a basic potassium calcium sulfate. Interestingly, the EDS spectrum shows no lead at all, but the other base elements, potassium and oxygen, are present. This issue may require further study if deemed of importance.

Samples 9 and 17 also contained small amounts of mercury, but the other constituents are similar to the rest of the writing and drawing inks. PLM examination of the samples did not show the presence of vermilion (mercury sulfide), a common red pigment, so its origin remains unknown.

All of the inks used for text or drawing were identified as iron gall inks. The variability of the amounts of iron present is not unusual in iron gall inks. We found no significant differences between the writing inks and the drawing inks used throughout the document and tentatively conclude that the text and drawings were most likely created contemporaneously. We did find one example in which paint was clearly over the writing; see Figure 7A.

The other black inks do show some differences.

Bulk analysis of Sample 15, the page number from Folio 26 Recto, includes elements common to the other inks but in different proportions (see Figure 15B). It also has a larger amount of iron than any of the text or drawing inks (see especially Figure 15C). This ink is an iron gall ink, but appears to be of a different formulation than the text and drawing inks.

Sample 19, the quire number, is a high carbon, very low iron ink. Microscopically, it appears as a transparent, light brown material without the particulate material suggestive of a carbon ink, and thus it is consistent with an iron gall ink of particularly low iron content. While a carbon ink cannot be completely ruled out, it is our conclusion that the ink present is simply an iron gall ink of particularly low iron content.

Sample 20 is from the "a" on Folio 1 Recto. The letter is somewhat faded, and the amount of ink available for sampling was very small. It is also a high carbon, very low iron ink. Again, its microscopical characteristics are consistent with an iron gall ink. Photomicrographs were made using both white light and ultraviolet fluorescence, which provided more contrast and readability (Figures 20A-1 through 20A-6). However, it

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does contain a number of larger particles; see Figures 20C through 20E. Figure 20C shows large amounts of calcium and phosphorus in roughly the same proportions, consistent with a particle of bone black. The other particles appear to be of mineral origin. The IR spectrum indicates the presence of a protein, not a gum. We suspect that the sample was contaminated with the proteinaceous substrate. A proteinaceous binder is unlikely.

Samples 19 and 20 appear to be different inks, although the small amount of material available from Sample 20 lowers the level of confidence in any conclusions we might wish to draw from the available data.

MEDIUM IDENTIFICATION

Infrared spectroscopy identified the binding medium of the writing and drawing inks as a gum; see the reference spectrum for gum Arabic (Figure 1D). The spectra include several sharp peaks in the region $1100\text{--}1000\text{ cm}^{-1}$ that are not expected for a gum as per the spectra in our library. This suggests the possibility of other constituents, which remain unidentified as of this date. Most recipes for iron gall inks include gum, usually gum Arabic, as an ingredient.

Gums were also identified as the binding media in the green paints. The blue and red-brown paints were not tested, but, as watercolors, gum would be likely.

BLUE PAINT

The blue paint was unambiguously identified as ground azurite with minor amounts of cuprite, a copper oxide. The red-brown particles visible in Figure 4A, the blue flower, are cuprite; PLM, EDS in the SEM and XRD were all in agreement on this identification. Infrared spectroscopy was not performed on either of the two blue paint samples, but a gum binding medium is the most likely, as consistent with the other samples tested.

CLEAR/WHITE PAINT

Sample 12, the clear/white material, was identified as proteinaceous (Figures 12B through 12D), with a large amount of calcium carbonate present. A mixture of glair (eggwhite) and calcium carbonate is likely.

GREEN PAINT

The green paint was tentatively identified as a copper and copper-chlorine resinate, most likely produced as a salted copper corrosion product. PLM indicated the presence

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of both isotropic green-stained transparent material consistent with copper resinate, and smaller amounts of anisotropic green particles. The presence of chlorine in the EDS spectrum suggests that the crystalline material might be atacamite or other copper-chlorine compound. In all cases, the amount of copper is in significant excess to that of chlorine, and something like a copper resinate, that is, a copper-containing amorphous organic material, is likely. X-ray diffraction of the sample produced no pattern whatsoever, strongly suggesting that the bulk of the material is non-crystalline.

None of the classical resins were found in this sample by IR spectroscopy, only the gum binding medium as was identified in all of the other paints and inks. Figures 3E and 3F are IR reference spectra for pine resin and mopa-mopa resin, respectively. It could well be that an excess of gum may be overwhelming the signal of a resin.

There are numerous medieval recipes for preparing a green copper pigment using common salt, such as Theophilus' *viride salsum*^{1, 2}.

RED-BROWN PAINT

The red-brown paint was identified as a red ochre by PLM and EDS in the SEM. XRD characterized the crystal phases present as consisting of hematite, iron sulfide, possibly minor amounts of lead sulfide and palmierite (a lead-potassium-sulfur compound (see Figure 8D) in, most likely, a gum medium.

CONCLUSIONS

- In all probability, the ink used for the text is the same as that used for the drawings; both are iron gall inks.
- In all probability, the other three inks, the one used for the page number, the quire ink, and the ink used to write the Latin alphabet on page 1R are all different from the text/drawing ink and from one another. Sample 15, the page number, is an iron gall ink; Sample 19, the quire number, is most likely an iron gall ink of low iron content, as is Sample 20, the "a".
- The blue paint is ground azurite.

¹ Eastaugh, N. *et al*, "Atacamite" in *Pigment Compendium, a Dictionary of Historical Pigments*, Elsevier (2004), page 27

² Theophilus, "Salt Green," Book I, Chapter 35, *On Divers Arts*, Dover Publications, New York, (1979), page 41

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- The green paint is a mixture of copper-stained amorphous organic material optically consistent with copper resinate, and copper-chloride compounds consistent with atacamite or similar compounds. No resins were identified in the green paint.
- The binding medium for all of the inks and the green paint is gum. The binder for Sample 20 is undetermined.

DISPOSITION OF THE SAMPLES

The samples taken from the manuscript were forwarded to Mr. Andreas Sulzer on 27 February 2009. We have retained the microscope slides and other specimen preparations in the event you may require further analysis.

Included with this report is a CD-ROM with the Adobe™ Acrobat file of this report.

Thank you for consulting with McCrone Associates. If you have any questions concerning any portion of this report, or should you require further analysis, please do not hesitate to call.

Sincerely,



Joseph G. Barabe
Senior Research Microscopist
Director of Scientific Imaging

JGB:jc

Enclosures

Ref: MA47613; retainer and Purchase Order dated 11/28/2008

TABLE I

Constituents Identified in *The Voynich Manuscript*

No.	Color & Item	Sample Locations		Constituents Identified	Figures
		Vertical	Horizontal		
1	Folio 26R Black ink from text	3.5 cm from top	10.2 cm from right	- Iron gall ink - Gum binder	1A–1D
2	Folio 26R Black ink from drawing	7.3 cm from top	5.5 cm from right	- Iron gall ink - Potassium lead oxide - Potassium hydrogen phosphate - Syngenite - Gum binder	2A–2D
3	Folio 26R Green leaf	14.2 cm from top	6.7 cm from right	- Copper – organic complex - Atacamite (possible) - Calcium sulfate - Calcium carbonate - Gum binder	3A–3F
4	Folio 26R Blue flower	2.3 cm from top	4.0 cm from right	- Azurite - Cuprite (minor)	4A–4C
5	Folio 26R Red-brown root	18.7 cm from top	9.1 cm from right	- Red ochre (hematite) - Lead oxide - Potassium compounds	5A–5C
6	Folio 47R Black ink from text	8.4 cm from top	12.6 cm from right	- Iron gall ink (low iron) - Calcium sulfate - Calcium carbonate - Gum binder	6A–6D
7	Folio 47R Green leaf	4.3 cm from top	5.4 cm from right	- Copper – organic complex - Atacamite (probable) - Gum binder	7A–7C
8	Folio 47R Red-brown root	0.8 cm from bottom	8.8 cm from right	- Red ochre (hematite) - Iron sulfide - Palmierite	8A–8D
9	Folio 78R Black ink from text	3.6 cm from top	12.7 cm from right	- Iron gall ink (low iron) - Calcium sulfate - Mercury compound (traces) - Gum binder	9A–9D
10	Folio 78R Blue water from pipe	7.4 cm from top	2.8 cm from right	- Azurite - Cuprite (minor)	10A–10C

TABLE I - continued

Constituents Identified in *The Voynich Manuscript*

No.	Color & Item	Sample Locations		Constituents Identified	Figures
		Vertical	Horizontal		
11	Folio 78R Green pool	3.6 cm from bottom	4.8 cm from right	- Copper – organic complex - Atacamite (probable) - Tin and iron compounds - Gum binder - Azurite and cuprite (traces)	11A–11C
12	Folio 78R Clear material from headdress of bather	3.6 cm from bottom	4.9 cm from right	- Calcium carbonate - Proteinaceous material, possibly eggwhite	11A, 12A-12D
13	Folio 86V Black ink from text	2.5 cm from top	6.7 cm from left	- Iron gall ink - Potassium compound - Calcium sulfate - Calcium carbonate - Gum binder	13A-13C
14	Folio 86V Black ink from drawing	4.0 cm from top	1.0 cm from right	- Iron gall ink (low iron) - Gum binder	14A-14C
15	Folio 26R Black ink from page number (26)	0.8 cm from top	0.8 cm from right	- Iron gall ink (high phosphorus and iron) - Gum binder	15A-15D
16	Folio 116V Black ink from text	6.9 cm from top	2.9 cm from left	- Iron gall ink (high iron) - Gum binder (no photograph recorded)	16A, 16B
17	Folio 70V Black ink from drawing (woman's face)	12.5 cm from top	14.3 cm from left	- Iron gall ink - Mercury compound - Titanium compound - Tin compound (particle) - Gum binder	17A-17F
18	Folio 70V Clear-white paint from drawing (woman's face)	12.5 cm from top	14.3 cm from left	- Proteinaceous - Carbohydrate – starch (traces)	17A, 18A, 18B
19	Folio 8V Black ink from quire mark on bottom right	0.2 cm from bottom	12.8 cm from left	- Iron gall ink (very low iron) - Gum binder	19A-19C
20	Folio 1R Black ink from "a" under chemical stain	2.5 cm from top	0.6 cm from right	- Iron gall ink (very low iron) - Bone black - Titanium compound - Binder undetermined	20A-1 – 20F