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Analysis of model iron gall ink and ink of 15th century manuscript by Raman spectroscopy

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In the work the Raman spectroscopy method was used in the study of model iron gall ink and ink of the ancient Russian manuscript codex of the XV century from the collections of the Department of Manuscripts of the Russian National Library (OR RNB). It should be noted that the closest in terms of the set of vibrational bands and relative intensities to the ink spectra of the manuscript were replicated inks made on the basis of tannins of gall nuts. The results of the study allow us to make an assumption about the type of ink of the ancient Russian manuscript codex of the XV century.

Keywords: iron-gallic ink, Raman spectroscopy, ancient Russian ink of the manuscript codex.

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Among cultural heritage objects, book monuments occupy a special place, and their study and preservation represent an important task. In the investigation of materials from ancient documents and manuscripts, various non-destructive spectral methods have found wide application. These include, for example, X-ray fluorescence, IR reflection spectroscopy, fiber-optic reflectance spectroscopy [1,2], Mössbauer spectroscopy [3], and electron paramagnetic resonance [4]. Raman scattering spectroscopy is among the primary methods for studying manuscript inks [2,5,6], due to its high sensitivity to various ink components. The main features of Raman spectra (Raman scattering spectra) for different types of manuscript inks are currently known; however, due to the great diversity of ink recipes and ingredients used in their production, no clear correlations exist between bands in the Raman spectra of inks and their composition, even for replicated inks. The task of identifying manuscript inks is complicated by possible structural changes during the natural aging of manuscript materials.

The aim of this work was to apply Raman spectroscopy for analyzing the inks of the Old Russian manuscript codex KB10/135 from the collections of the OR RNB and to conduct a comparative analysis with spectra of model iron-gall inks. This manuscript is dated to 1467 (call number KB10/135, Gospel (of Luke and John), commentary by Theophylact of Bulgaria, Moscow).

Raman spectra of ink samples were recorded using a SOL Instruments Raman microscope (model Confotec® MR350, Belarus). For excitation of Raman spectra, a solid-state laser with a wavelength of 785 nm was used in backscattering geometry. The laser power on the ink sample was about 1 mW. Spectra were recorded using a 40 lens. The laser spot size on the sample was $\approx 1.7\,\mu$m. The accumulation time for a single spectrum was 10 s, with 5–10 repetitions. Raman spectra were recorded with a 600 mm^{-1} grating in the Raman shift range 100–1740 cm^{-1}. This range captures the main vibrational bands of iron-gall inks in Raman spectra. The spectral resolution of the instrument was approximately 2.33 cm^{-1}.

For each selected page of the manuscript, ink measurements were taken at multiple locations on both single letters and different letters. Raman spectra of model inks applied to cotton paper were also measured at multiple locations.

Investigation of 15th-century manuscript inks

The inks of the 15th-century manuscript were investigated on six pages (70 verso, 99 verso, 175, 283, 284, 453) using the Raman scattering method. Fig. 1 shows the Raman spectra of inks from manuscript KB10/135, measured on page 70 verso at four different locations on the page. In the Raman spectra of inks on this page, the following bands are observed: at 1581, 1482, 1394, 1336, 1286 (narrow), 705 (narrow), 645 (narrow), composite in the 640–500 cm^{-1} range, around 400 and 230 cm^{-1} [1]. In addition to these bands, less intense and pronounced bands are observed around 1435, 1220, 1170, 1100, 960, 815, 780 cm^{-1}. The interpretation of several bands is presented in the table.

From the spectra, it is evident that the listed bands are present in the Raman spectra of all inks, with differences lying in signal intensity, spectral resolution, and band intensity ratios. From Fig. 1, it can be seen that the band around 1435 cm^{-1} is poorly resolved in the least intense spectrum. Note that visible differences in the Raman spectra

Frequencies of bands in Raman spectra of manuscript inks and model inks with interpretation of some bands

Raman shift, cm^{-1}	Intensity[1]	Frequency, cm^{-1}	Interpretation from literature[5,9]
Manuscript		Model	
1581	str.	1584	oscillation mode *8a* of the benzene ring; intensity decreases upon complex formation
1482	str.	1485	oscillation mode *19a* of the benzene ring; ν(C–O) and δ(C–H); sensitive to acidity pH
1435	w.	1436	symmetric vibrations of the –COO–group (carboxylate –COO–)
1394	str.	1400	symmetric vibrations of the –COO– group (carboxylate –COO–)
1336	str.	1340	in-plane stretching of the aromatic ring, ν(C–O) and δ(C–H); sensitive to polyphenol structure and acidity
1286	med. narrow	1286	vibrations ν(C–O) and δ(C–H)
1220	weak		vibrations ν(C–O) and δ(C–H)
1170	w.	1170	
1100	w.	1114	ν(C–O) and δ(C–H)
960	w.	930	
815	w.	815	
780	w.	780	
705	med. narrow	705	
645	med. narrow	645	stretching vibrations of the Fe–O bond ν(Fe–O)
610	med.	600	ν(Fe–O)
540	med.	540	ν(Fe–O)
400	str.	400	ν(Fe–O)
230	w.		

[1] Notation: weak — weak, med. — medium, strong — strong.

of inks on page 70 verso are observed in the 640–500 cm^{-1} frequency range. The complex band in this range represents the sum of at least two bands at 610 and 540 cm^{-1} with an arm around 485 cm^{-1}. In the most intense spectrum, an additional band appears at 570 cm^{-1}. Fig. 2 shows the Raman spectra of inks from manuscript KB10/135, measured on page 283 at three locations. The spectra of inks on this page contain the same bands as those on page 70 verso. From Fig. 2, it can be seen that the band around 1435 cm^{-1} is poorly visible in all presented Raman spectra of inks on page 283. We emphasize the small difference in intensity of the Raman spectra of inks on page 283 and note the presence of a band with a similar contour in the 680–500 cm^{-1} frequency range. This band represents the sum of two bands at 600 and 540 cm^{-1} with similar intensities.

Measurements of Raman spectra on the other four pages showed the presence of the same vibrational bands as in the spectra on pages 70 verso and 283. Despite the similarity of band sets in the Raman spectra of the investigated inks, some differences are observed both within a single page and across different pages. The main differences are related to varying intensities. It is also worth noting the variation in intensity of bands at 1435 and 1400 cm^{-1} and changes in the intensity ratios of the complex band 680–470 cm^{-1}.

Investigation of model inks

To understand and interpret the molecular spectra of manuscript inks, Raman spectra of model inks were measured. Model inks are inks prepared according to ancient recipes with various components in their composition [7]. Ink samples were prepared based on tannin extracts obtained from oak gall infusions and alder bark decoctions. To obtain polyphenol-iron complexes, rusted iron or iron vitriol was used. Cherry gum was added as a binder. In addition to the listed substances, other components present in Old Russian ink recipes were also added. In [8], differences in Raman spectra of inks prepared from tannins from different sources — oak galls and alder

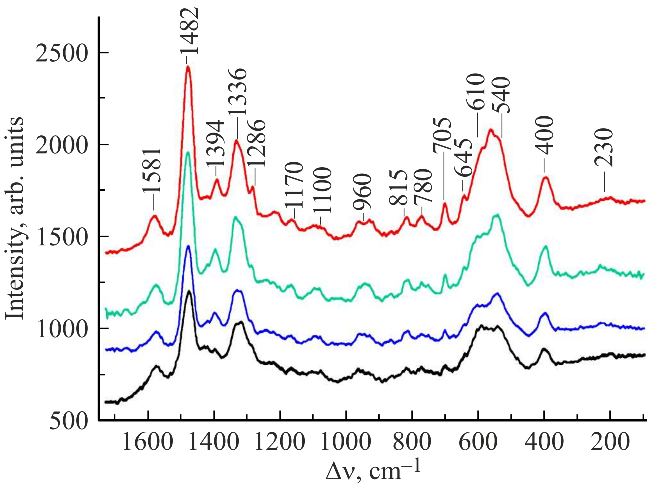

Figure 1. Raman spectra of inks from manuscript KB10/135 on page 70 verso in four different letters.

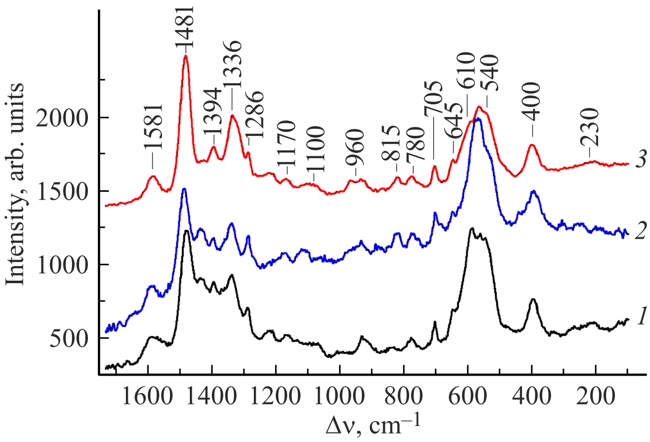

Figure 3. Raman spectra of replicated inks N 9 (*1*) and N 3.9 (*2*), prepared based on oak gall infusion and applied to cotton paper, and manuscript KB10/135 inks on page 70 verso (*3*).

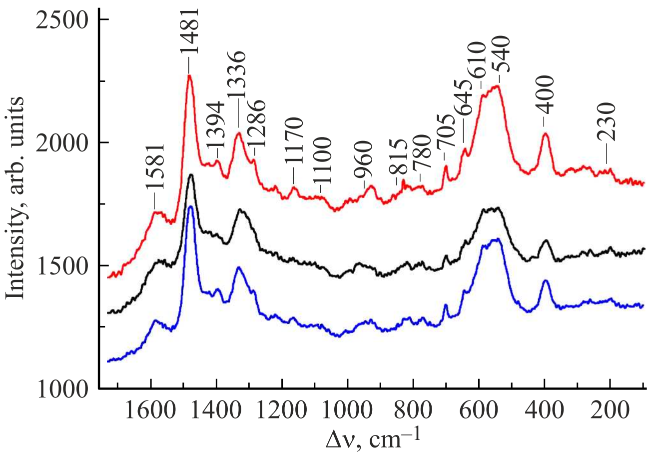

Figure 2. Raman spectra of ink samples from manuscript KB10/135 in three different letters on page 283.

bark—were demonstrated on model samples. For example, in the Raman spectra of inks based on oak gall infusions, bands around 400 cm^{-1}, 1340 and 1288 cm^{-1} and bands around 1487 and 1584 cm^{-1} were identified. In the spectra of inks based on alder bark decoction, a doublet around 1270 and 1315 cm^{-1}, a band with a maximum at 1482 cm^{-1} and a broad band around 1560 cm^{-1}were observed.

Fig. 3 shows Raman spectra of replicated ink samples. Sample N9 was prepared based on oak gall infusion, rusted iron with the addition of cherry gum [8]. In the Raman spectrum of these inks, a band around 400 cm^{-1}, a broad complex band in the 500−640 cm^{-1} region, and intense bands at 1340, 1400, 1436, 1485 and 1584 cm^{-1} can be noted. Additionally, less intense bands are observed at 1286 (narrow), 1225, 1170, 1114, 930, 815, 705 (narrow), and 645 cm^{-1}.

The broad band in the 500−640 cm^{-1} region represents the sum of two bands at 600 and 540 $cm^{-1}$with nearly equal intensities and a slight predominance of the band at 600 cm^{-1}. Sample N 3.9 was prepared based on oak gall infusion, rusted iron with the addition of gum and honey. In the Raman spectrum of sample N 3.9, an additional band at 565 cm^{-1} is visible. The frequencies of bands in the Raman spectra of model inks are listed in the table. Note that the weak band around 1100 cm^{-1} may partially be associated with scattering from the substrate — cellulose. For comparison, Fig. 3 also shows the Raman spectrum of manuscript KB10/135 inks (page 70 verso). The similarity of the ink spectra is evident both in band positions and intensity ratios.

It is known that gallic acid, tannic acid, and pyrogallol are components of the aqueous extract of oak gall infusion. Experimental Raman spectra of iron complexes of these compounds and quantum chemical calculations of vibrations of the gallic acid-iron complex have shown that the three most intense bands appear in the ranges 1450−1490 cm^{-1} (ν_1), 1320−1345 cm^{-1} (ν_2) and 400−650 cm^{-1} (ν_3), which are characteristic of polyphenol-metal complexes [5,9].

The ν_1 band appears in the frequency interval 1485−1465 cm^{-1}, with its position depending on the phenol structure. This band can be attributed to the benzene vibrational mode 19a, C−O bond stretching vibrations (ν(C−O)) and C−H deformation vibrations (δ(C−H)). The band is low-intensity in phenols not involved in complex formation.

The ν_2 band can be seen in the frequency interval 1345−1295 cm^{-1} and is associated with in-plane stretching of the aromatic ring, bond stretchingν(C−O) and deformation δ (C−H). The band position is sensitive to the polyphenol structure, with frequency increasing in the series tannic acid > gallic acid > pyrogallol. Both ν_1 and ν_2 bands are sensitive to acidity pH, but the ν_1 band is more sensitive.

The band at 1580 cm^{-1} is attributed to the *8a* mode of the benzene ring, whose intensity significantly decreases upon complex formation with metals.

The band at $1430\,cm^{-1}$ and possibly at $1395\,cm^{-1}$ is associated with symmetric vibration of the $-COO-$group. These bands appear in the Raman spectra of tannic and gallic acids due to the presence of carboxylate $-COO-$ in their structure and are absent in the pyrogallol spectrum.

The weak doublet at $1299/1217\,cm^{-1}$ and the broad band at$1100\,cm^{-1}$ can be attributed to vibrations $\nu(C-O)$ and $\delta(C-H)$. These bands can be used for identifying phenolic compounds in inks due to their sensitivity to substituent positions in aromatic rings.

The ν_3 band is associated with valence vibrations of $Fe-O$ bonds ($\nu(Fe-O)$), formed by the interaction of iron with oxygen in polyphenolic compounds. $\nu(Fe-O)$ vibrations can appear over a broad frequency range $650-400\,cm^{-1}$ due to various interactions of the iron cation with oxygen atoms in polyphenols. For example, in the Raman spectra of iron-tannic acid complexes or other polyphenols, $\nu(Fe-O)$ bands can be observed at 650, 600−595, 560−550 and $400\,cm^{-1}$. The interpretation of several bands is given in the table.

Comparison of the Raman spectra of the manuscript and model inks showed that the inks prepared based on oak gall tannins were most similar to the manuscript ink spectra in terms of band sets and relative intensities.

Conclusion

The results of the investigation of inks from a 15th-century Old Russian manuscript codex revealed that Raman spectra of the manuscript inks on six pages show similar band sets at 1580, 1485, 1340, 1290, 705, 645, composite in the 640−500 range, around 400 and $230\,cm^{-1}$. In addition to these bands, less intense bands are observed at 1435, 1400, 1220, 1180, 1100, 960, 815, $780\,cm^{-1}$. It was found that the Raman spectra of manuscript inks exhibit scatter related to varying spectral intensities and some changes in relative band intensities. This particularly concerns the complex band in the $680-500\,cm^{-1}$ region, formed by $Fe-O$ bond vibrations $\nu(Fe-O)$ in the organometallic complex.

Comparison with Raman spectra of inks based on oak gall tannins allows the inks on the investigated pages of manuscript KB10/135 to be classified as iron-gall inks prepared using oak gall tannins, based on the band sets and their relative intensities.

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Conflict of interest

The authors declare that they have no conflict of interest.

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