

# RGB Approach for Pixel-Wise Identification of Cellulose Nitrate Photo Negative Yellowing

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## *For section 2 (Raman spectroscopy)*

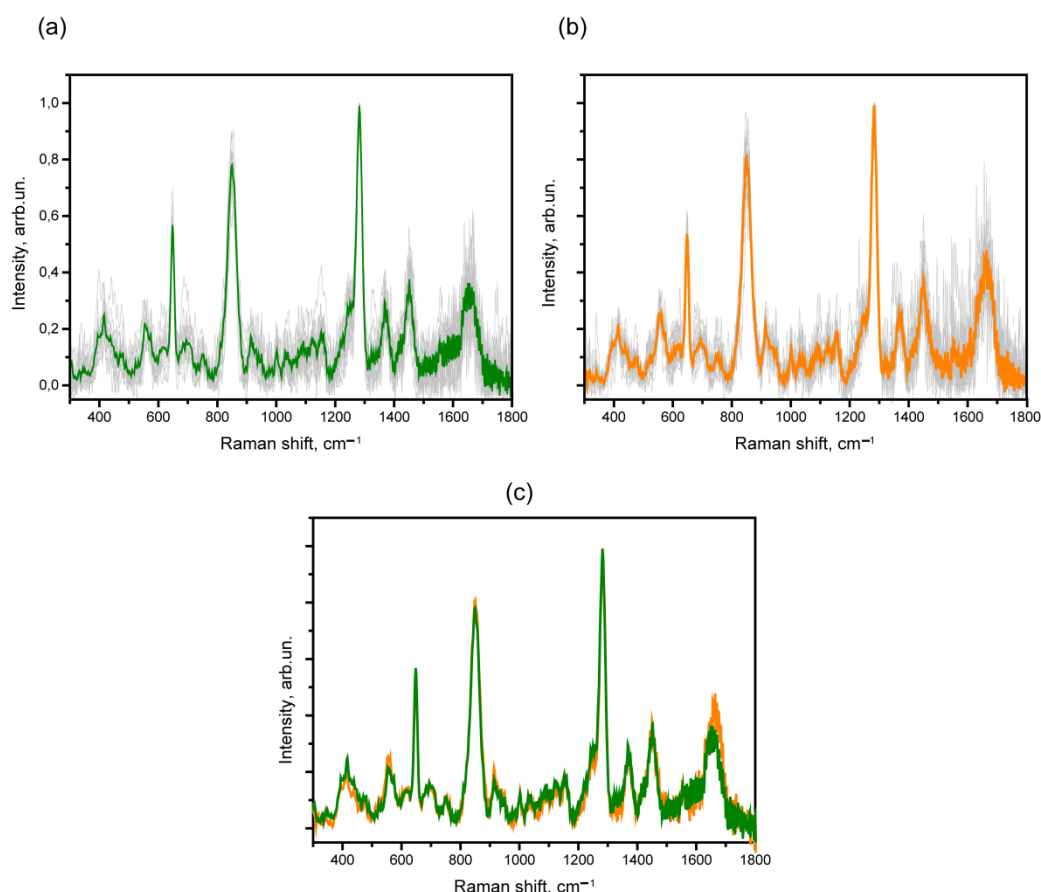
In order to identify degradation of the cellulose nitrate base, the Raman spectroscopy method was used. This method was chosen due to the layered structure of the photo negative sample, its upper layer consists of a relatively thick gelatin layer. This upper layer does not allow using the IR absorption spectroscopy approach in the mid-IR range. The obtained Raman spectra from 20 normal and 20 yellowed control samples were checked for degradation of the base for studying the statistical dependence.

They showed intense peaks associated with the NO<sub>3</sub> group in cellulose nitrate, namely 850 (related to  $\nu(\text{N-O})$ ) and 1282 cm<sup>-1</sup> (related to  $\nu_s(\text{NO}_2)$ ). In addition, the spectrum contained a peak near 650 cm<sup>-1</sup>, related to camphor, typical for celluloid [1]. It should be noted that the control sample was made up of negatives from Raman spectra that had a similar composition, which was manifested in a close peak ratio and the absence of other inorganic inclusions.

An increased intensity of the band in the range of 1600-1700 cm<sup>-1</sup> was noted in the spectra obtained for yellowed samples, related to the stretching vibrations in the C=O bond. This coincides with the model experiments on cellulose nitrate samples given in [4].

## *Raman spectroscopy experimental part*

Raman spectra were obtained in backscattering geometry using the portable Raman spectrometer Bravo (Bruker Corporation, Billerica, MA, USA). The resolution was about 10 cm<sup>-1</sup>. The laser spot diameter was about 1 mm. The laser power was 100mW. The accumulation time was 3 s. The spectra were obtained in the spectral region of 300-1800 cm<sup>-1</sup>. The baseline correction and further intensity normalization was performed within the OriginPro2021b (OriginLab Co.; Northampton, MA, USA) software.



**Figure S1.** Raman spectra obtained from each of the 20 normal negatives (gray), as well as the average spectrum (green) (a); Raman spectra obtained from each of the 20 yellowed negatives (gray), as well as the average spectrum (orange) (b).

For section 2.3. (data processing)

**Table S1.** Estimates of the upper and lower ranges limits in absolute and idealized scales. Values in the table are rounded to the nearest whole number.

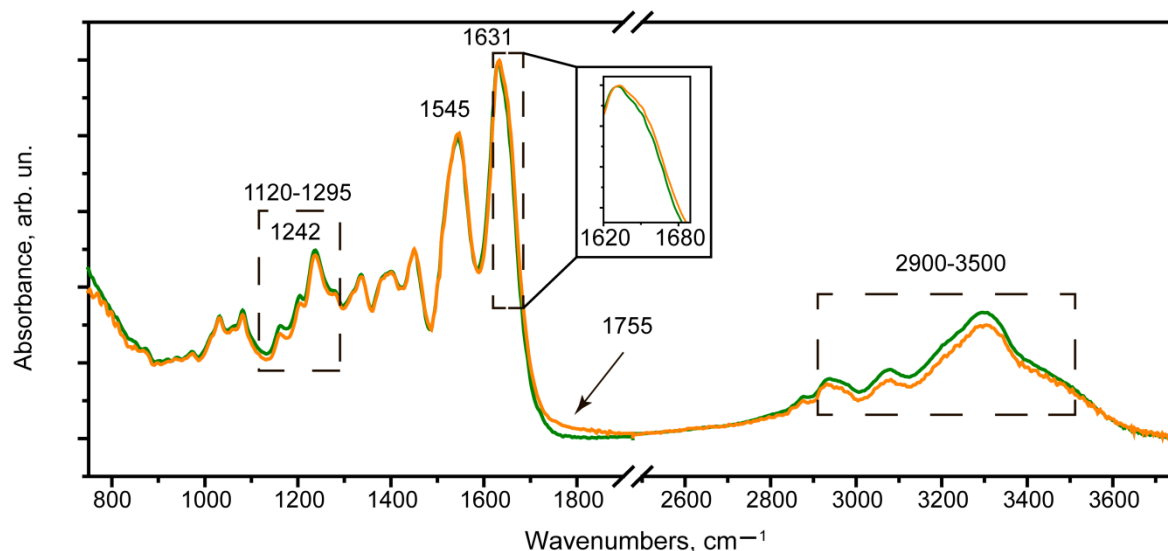
№*	Normal group					Yellowed group				
	Caver,white	Gabs_bottom	Gabs_top	Gideal_bottom	Gideal_top	Caver,white	Gabs_bottom	Gabs_top	Gideal_bottom	Gideal_top
1	198	31	110	40	142	210	33	179	40	217
2	207	38	175	47	216	210	37	162	45	197
3	237	30	189	32	203	216	41	149	48	176
4	226	37	172	42	194	210	20	179	24	217
5	196	46	127	60	165	209	25	153	31	187
6	224	28	148	32	168	222	23	161	26	185
7	244	17	165	18	172	224	35	149	40	170
8	205	28	154	35	192	218	30	166	35	194
9	203	35	175	44	220	213	10	147	12	176
10	218	36	136	42	159	199	26	181	33	232
Mean±STD				39±11	183±26	Mean±STD				33±11 195±21

\* this number does not mean that the same number (negative) corresponds to both the upper and the lower limits. The set of negatives used to evaluate the lower limit are the so-called dark negatives within the normal or yellow group. The sets for evaluating the upper limit are the so-called light negatives within the normal or yellow group.

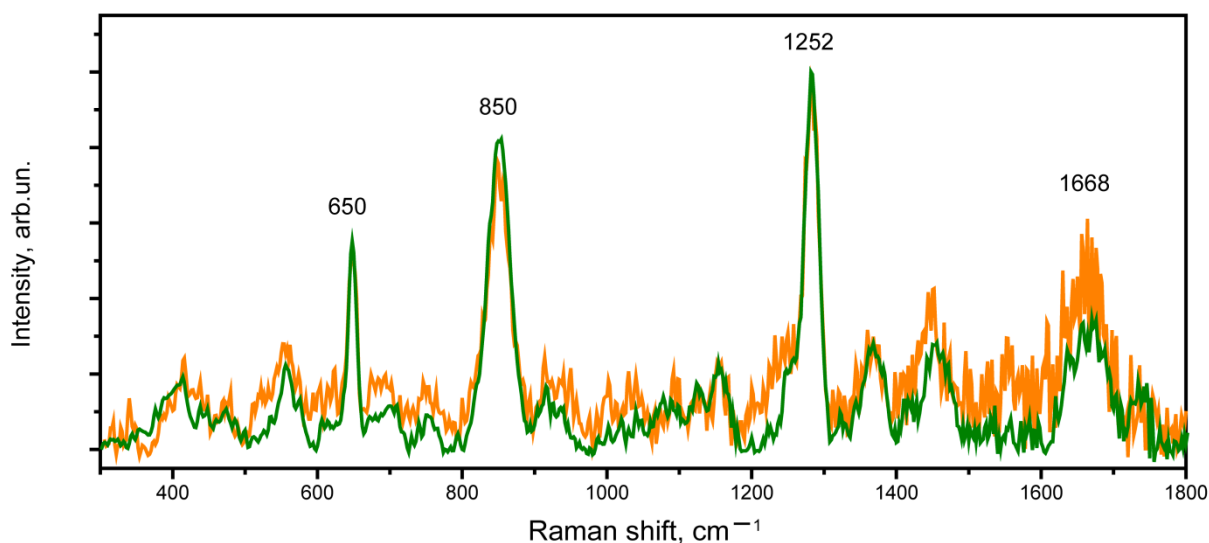
For section 3.4 (Application approach)

Before studying the possibility of differentiating between normal and yellowed areas on a particular photographic negative, the composition was checked by Raman spectroscopy and ATR-FTIR spectroscopy. The result is shown in Fig. S2.

(a)



(b)



**Figure S2.** FTIR absorption spectra from normal (green) and yellowed (orange) regions (a), Raman spectra from normal (green) and yellowed (orange) regions (b). The main peaks mentioned in the article are labeled. For comparability the absorbance and intensity were normalized. In case of Raman spectra the background was subtracted.

Caused by various factors (temperature, exposure to UV radiation), the process of degradation of the main chain of cellulose nitrate occurs, as well as the splitting off of  $\text{NO}_2$  groups for the side chain with the formation of  $\text{C}=\text{O}$  bonds [4,31]. In the IR absorption spectra, this is manifested by an increase in the peak at about  $1740\text{ cm}^{-1}$ , caused by stretching vibrations in this bond. In addition, it is worth noting that the direct process of degradation of the cellulose nitrate base is accompanied by degradation in an aggressive environment and adjacent layers, which in our case is a gelatin layer, also occurring with the formation of  $\text{C}=\text{O}$  bonds [32]. The formation of  $\text{C}=\text{O}$  bonds is manifested not only in the IR absorption spectra, but also in the electronic absorption spectra of the electronic

transition of the  $n \rightarrow \pi^*$  type, its wavelength is in the range of 300–350 nm. This leads to an increase in absorption (or a decrease in reflection) in the blue-violet region of the spectrum at the border with the UV region. Such a reduced reflection leads to a smaller ratio of B/G and B/R components specifically for the yellowed areas, which allows us to associate these ratios with the yellowed areas. Due to the greater photoresponse of typical silicon detectors used in cameras, namely to photons with the energy of the blue and green

#### *FTIR spectroscopy experimental part*

IR absorbance spectra were obtained at microscope-type FTIR spectrometer Lumos II (Bruker; Billerica, MA, USA) with the ATR accessory. The focusing was performed with the help of 20x mirror objective. The detector was TE-MCT detector with Peltier cooling system. The resolution was  $4 \text{ cm}^{-1}$ . The number for scans was 100 items. The (0,1) normalization was performed within the OriginPro2021b (OriginLab Co.; Northampton, MA, USA) software.