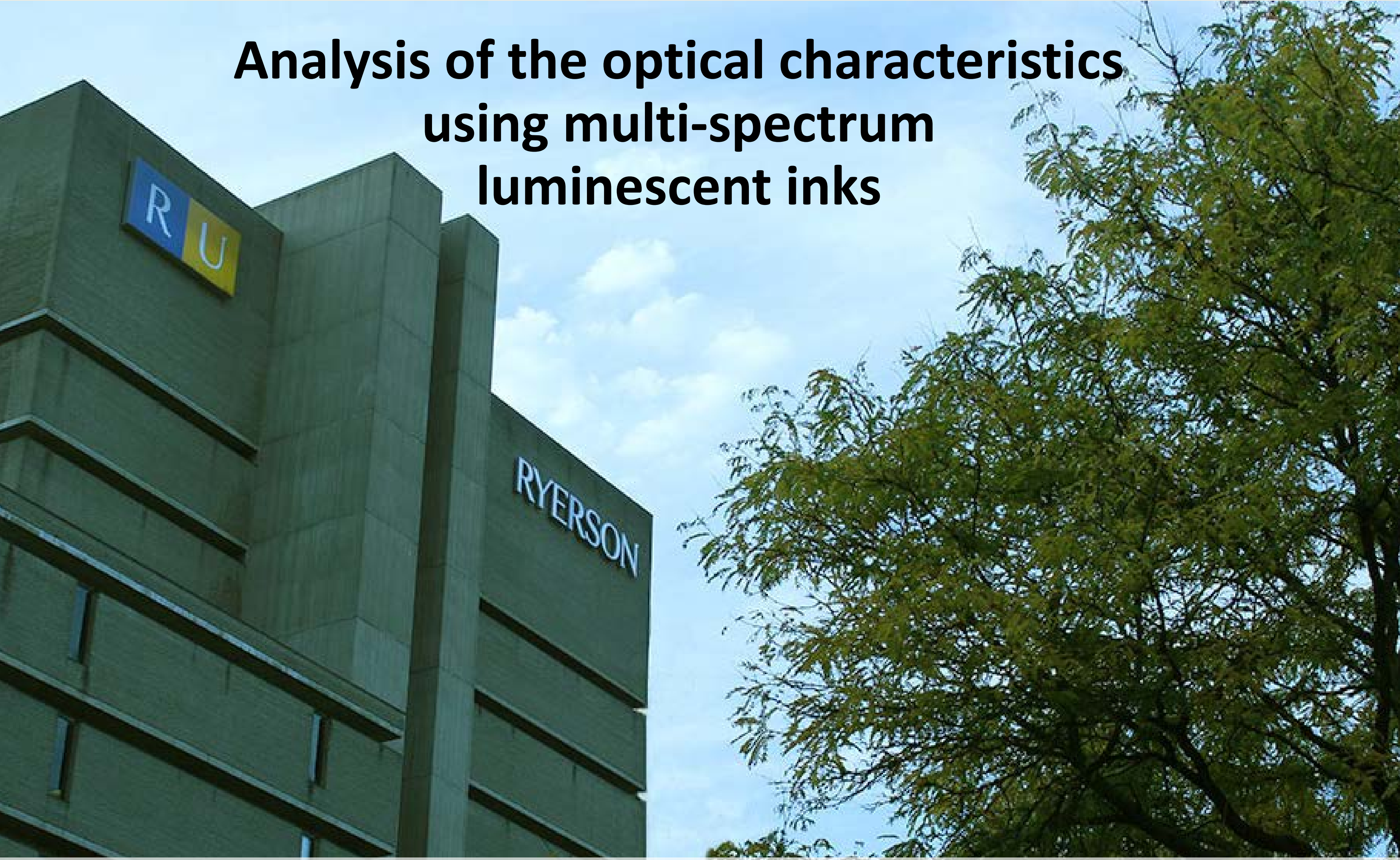
# Analysis of the optical characteristics using multi-spectrum luminescent inks





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# Introduction into the multi-spectrum luminescent inks research

- **Luminescence** is emission of surplus energy in the form of light caused by induction.
- A large group of gaseous, liquid, and solid, organic and inorganic materials are luminescent in nature (depends on the physical state of the material and induction type).
- The luminescence effect is applied in information visualisation, electronic and microelectronic products, light techniques, etc.
- **Luminophore** is a substance that exhibits the phenomenon of luminescence.
- Luminophores are used to cover continuous or targeted surfaces or to modify materials.

# Introduction into the multi-spectrum luminescent inks research

- Luminophore absorption and emissivity are associated with **Stokes-Lommel** law, stating that the wavelength of photoluminescence is greater than the wavelength of the exciting light.

- For instance, after UV luminophore is exposed
  $\lambda$ = 254 nm, $\lambda$ = 312 nm or $\lambda$ = 365 nm,
  it emits visible light.

- There is an exception to Stokes-Lommel law, the so-called **'anti-Stokes' luminophores**, when induced by IR (Infrared, $\lambda$ = 980 nm exposure) emit a visible light.

- Luminescent printing inks have 'Stokes and anti-Stokes' features.

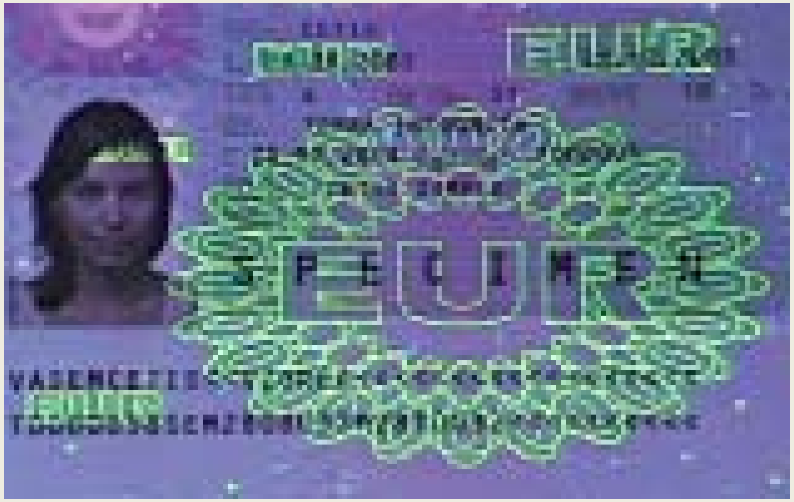
# Introduction into the multi-spectrum luminescent inks research

- In printing, luminophores are used for:
  - product-authentication tags,
  - document security features,
  - logotypes,
  - brands

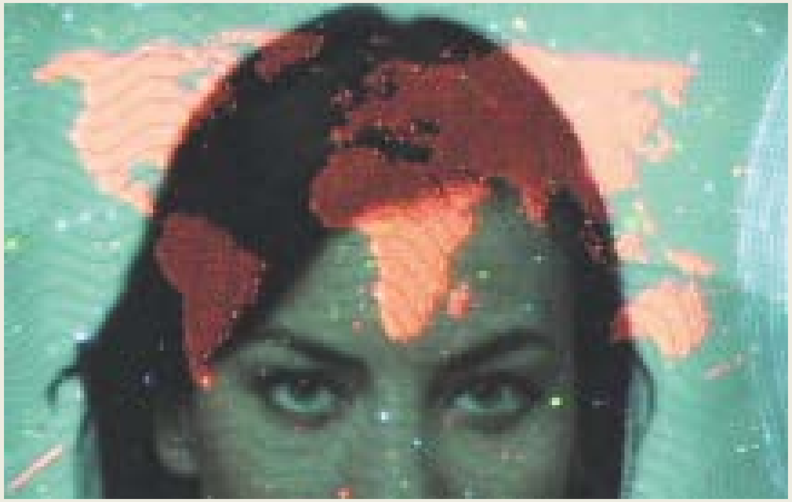
- In the production process, the above mentioned products are affected by **high temperature**
- The inks are covered with a transparent **polymer coating or a lacquer**.
- All these affect the intensity and wavelength of the luminescence emission.
- The luminescence intensity and wavelength diffusion rate is an important feature of the product, especially when these parameters are used for authenticity check.

# Fluorescent inks, used in printing protective elements, are invisible in daylight and become visible in UV light only

- Ultraviolet light activates the luminance of fluorescent (UV) inks

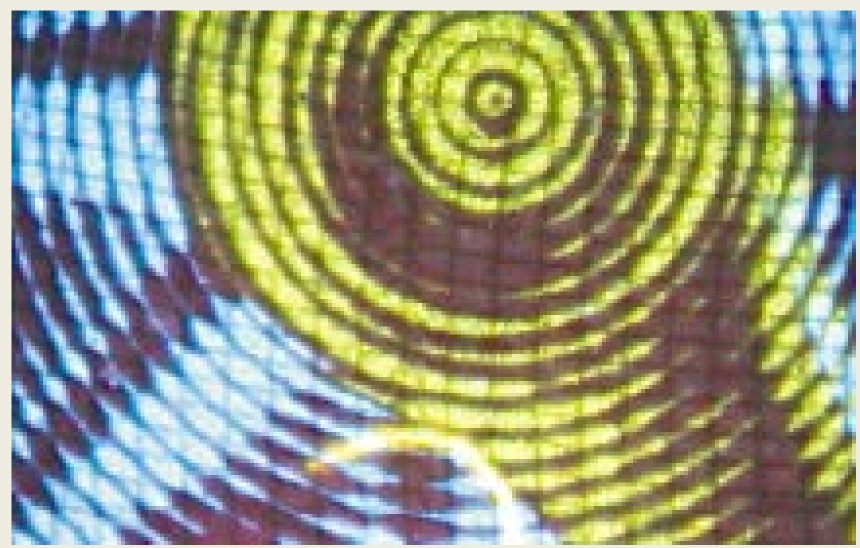



- UV fluorescent ink in the area of the photo



UV Fluorescent colours, used in printing security elements, are invisible at daylight and become visible under UV light.
They are divided into: ¥ fluorescent and ¥ bi-fluorescent colours.

- Ultraviolet light provokes fluorescent (UV) colours to glitter.
- ¥ fluorescent colours  glitter under illumination using a long-wave ultra-violet light.
- ¥ bi-fluorescent colours glitter under illumination using a long-wave or short wave ultra-violet light.

# Introduction into the multi-spectrum luminescent inks research

- The luminescent inks with UV and IR exposure excitation have been introduced into the printing industry recently.

- Spectroscopic and colorimetric analysis aims to assess the change of the optical parameters of the luminescent inks under different UV ($\lambda$ = 254, 312, 365 nm) and IR ($\lambda$ = 980 nm) wavelength exposure.

- Experiments aim to combine the two (Stokes and anti-Stokes) principles of luminescence.

# Methods and equipment

In order to evaluate luminescent printing inks, it is necessary to identify major controllable physical criteria:

1. Spectrum emission (spectrum composition and distribution of energy exposure wavelengths);

2. Absorption spectrum (dependence of the absorption coefficient on the wavelength);

3. Luminescence intensity ratio (excitation and exposure energy rate);

4. Kinetics of the luminescence process (change of luminescence intensity based on external influences).

# Methods and equipment

- During the process of the material illumination occurs movement of the electrons from one energy level to another.
- The distance between energy levels depends on the structure of molecules.
- Part of the exposure energy *E0* is consumed for temperature, absorption and other processes (w),
- The other part is emitted in the form of the photons.
- Exposure of the photon energy will always be lower than emitted (hv), therefore energetic luminescence expression obtains the following form:

$$E0 - E1 = hv^{*} + w$$

h – Planck's constant,

v* – absorbed light oscillation frequency.

# Methods and equipment

- It is inconvenient to evaluate the efficiency/quality of luminescence using energy levels, thus the intensity of light is used as measure.
- The sample of the luminescent ink QFX was analysed using the videospectral comporator *Foster + Freeman* model VSC5000 – an automated system of the print analysis (*Fig.1*).


*Fig. 1. Video spectral comporator VSC5000*

# Methods and equipment

- Various wavelength λ of exposure were used for the sample illumination:
  - 254 nm
  - 312 nm
  - 365 nm
  - 980 nm

- Luminescence measurements were performed on the print samples including plain paper and paper covered with a 50 µm PC laminating coating.

# Methods and equipment

- Laminating coating has an impact on the change of the luminescence characteristics.
- The laminating technology is related to thermal effects. The hot embossing requires temperature range 90–110 °C.
- The issue of the thermal effect becomes more urgent when the product is multi-layered, e.g. identification cards (ID) that may have five or more layers. The layers are collated and fused under pressure at high temperature until polymer reaches a glass transition temperature.
- Presently, the production of ID cards widely employs polycarbonate (PC) with glass transition temperature – 170–200 °C (compared to the other polymer is relatively high).

# Methods and equipment

- Experiments were carried out to determine different effects of temperature on the characteristics of the luminescence emission.

- The experiments involved the analysis when the samples were heated by the controllable temperature source. The spectra were measured by the comporator VSC5000.

- Results were analysed using spectrogram I = f (λ), chromaticity x–y diagram and CIE L * a * b evaluation system

# Outcomes of the analysis

- QFX inks combine Stoke and anti-Stoke luminescence, induced by UV and IR exposure: typically wavelengths: 254 nm, 312 nm and 365 nm, and the anti-Stokes luminescence at 980 nm.

- The main parameters characterizing the efficiency of inks are:

  1. Intensity of the luminescence emission;

  2. Contrast of the transmitted light wavelength.

- Samples of the spectrogram at UV and IR exposure without protective coatings and with a 50 μm PC coating are shown in Fig. 2.

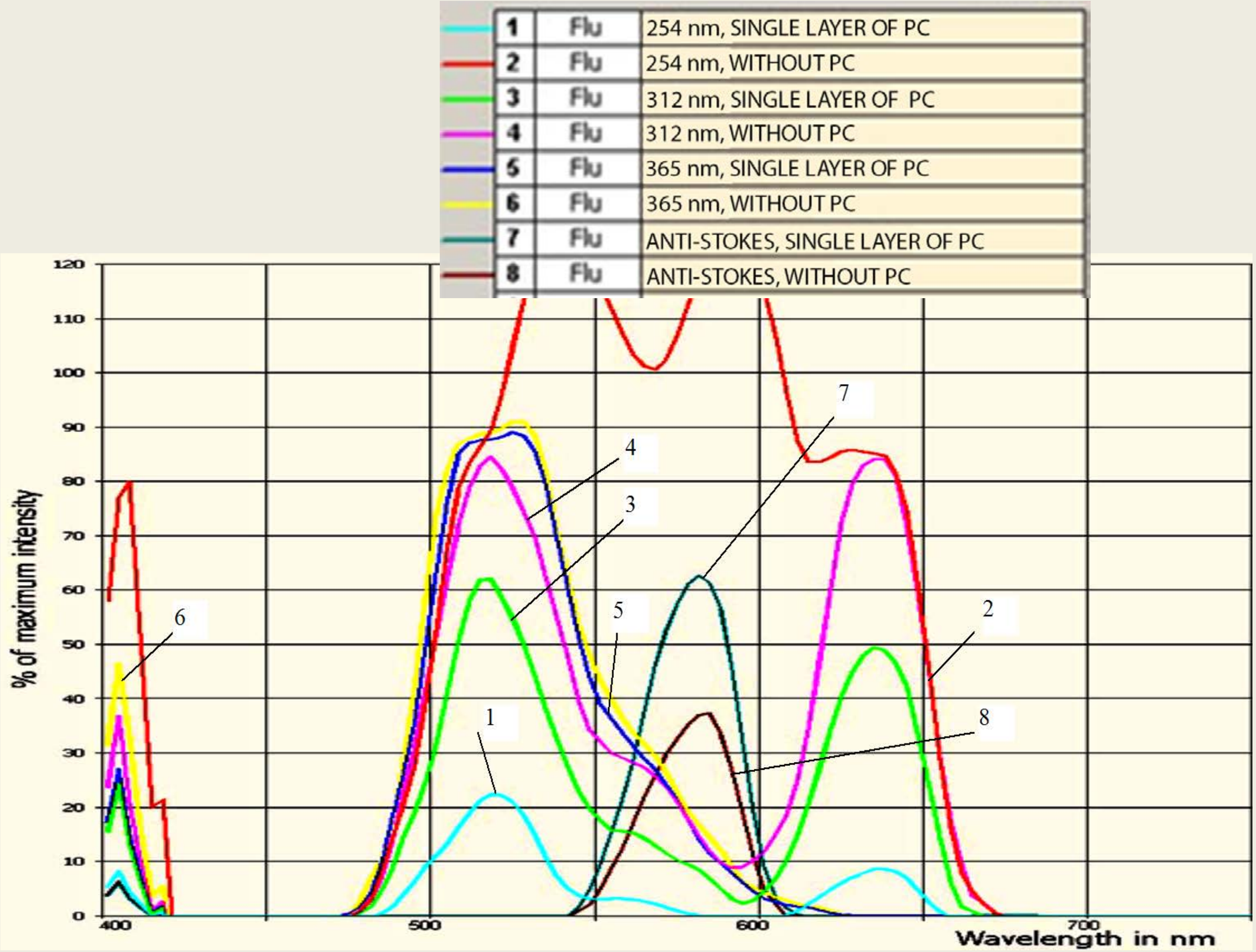



Fig. 2. The spectrogram of the sample lumiscence.
UV exposure – 245 nm, 313 nm, 365 nm; IR exposure – 980 nm.
Spectrogram – 1, 3, 5, 7 – with a 50 µ PC laminating coating;
2, 4, 6, 8 samples without coating.

# Outcomes of the analysis: spectrum

- It is evident from the Fig. 2 that using of the three different wavelengths UV and IR luminescence exposure, the spectra are not in a particular range, but they consist of several different λ components.

- It means that visually observed colour is not a part of the colour spectrum, but a mix of two or three colours:

  410 nm (blue colour),

  520–570 nm (green colour),

  640 nm (yellow colour).

- Such distribution of the luminescence spectrum does not produce a solid contrasting colour.

# Outcomes of the analysis: intensity

- Protective coating reduces the intensity of the luminescence emission and width of the spectrum.
- Decrease in the luminescence spectrum depends on the wavelength of luminescence exposure:
- In the presence of the exposure at 254 nm, the luminescence emission is reduced 6 times;
- Exposure up to 312 nm – luminescence through the PC protective coating is reduced up to 0.65 times compared with the luminescence without a coating.
- Exposure of 365 nm – the coating has almost no effect on the intensity of the luminescence emission.
- At the anti-Stokes luminescence (980 nm exposure), a PC coating decreases the emission intensity approximately by 0.6 times.

# Outcomes of the analysis: intensity

- The intensity of the luminescence UV emission largely depends on the exposure wavelength.
- Maximum intensity of the luminescence emission is produced at 254 nm exposure.
- The average $\lambda = 312$ nm and $\lambda = 365$ nm UV exposure causes a similar intensity of the luminescence. However, its intensity is about 0.7 times smaller than at the 254 nm exposure.
- Very similar results are obtained at 980 nm exposure (anti-Stokes luminescence). The luminescence intensity decreases approximately 10 % compared with the 365 nm exposure.
- The luminescence spectra are measured as the surface is covered with a 50 µm polycarbonate (PC) coating under the same exposure conditions.

# Outcomes of the analysis: x-y diagram

- Luminescence spectral change is an undesirable phenomenon for the authentication control. Especially when luminescence colours are very thin at the different exposure and the protective PC coating alters its optical characteristics.

- It is impossible to apply some wavelengths of the UV exposure for any sophisticated graphics solutions at low contrast.

- Low luminescence contrast in different wavelengths of exposure is demonstrated in the chromaticity *xy* diagram (Fig. 3).

# Outcomes of the analysis: x-y diagram

- Visible luminescence colours are shown in the chromaticity x-y diagram (Fig. 3).

- As the marked comporator VSC5000 points in the chromaticity x-y diagram demonstrate, the dominant colours of the luminescence emission are green and yellow (contrary to the provided characteristics by the manufacturer).

- Visible luminescence colours are visually similar and close within the optical range as evident in the chromaticity x-y diagram

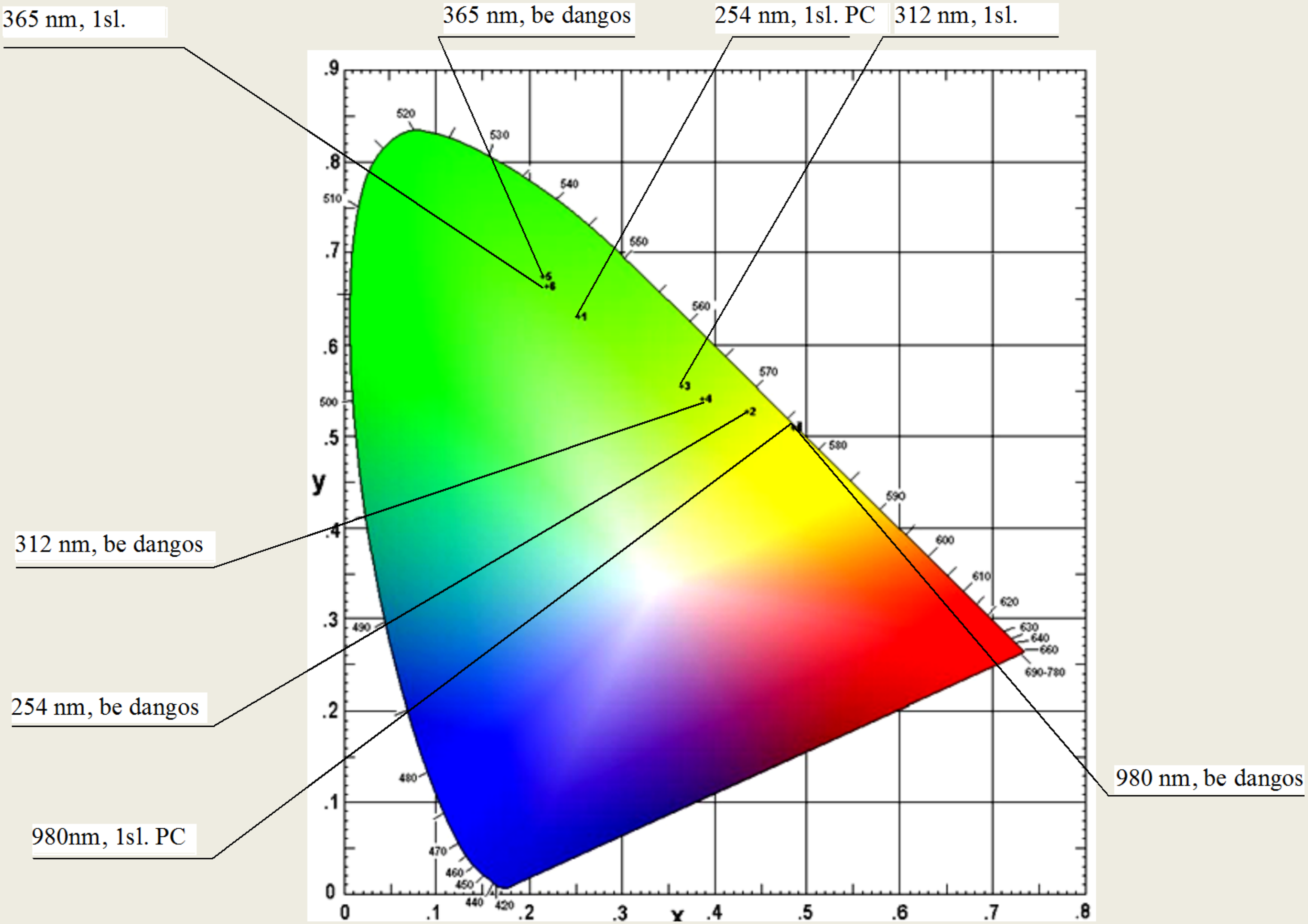
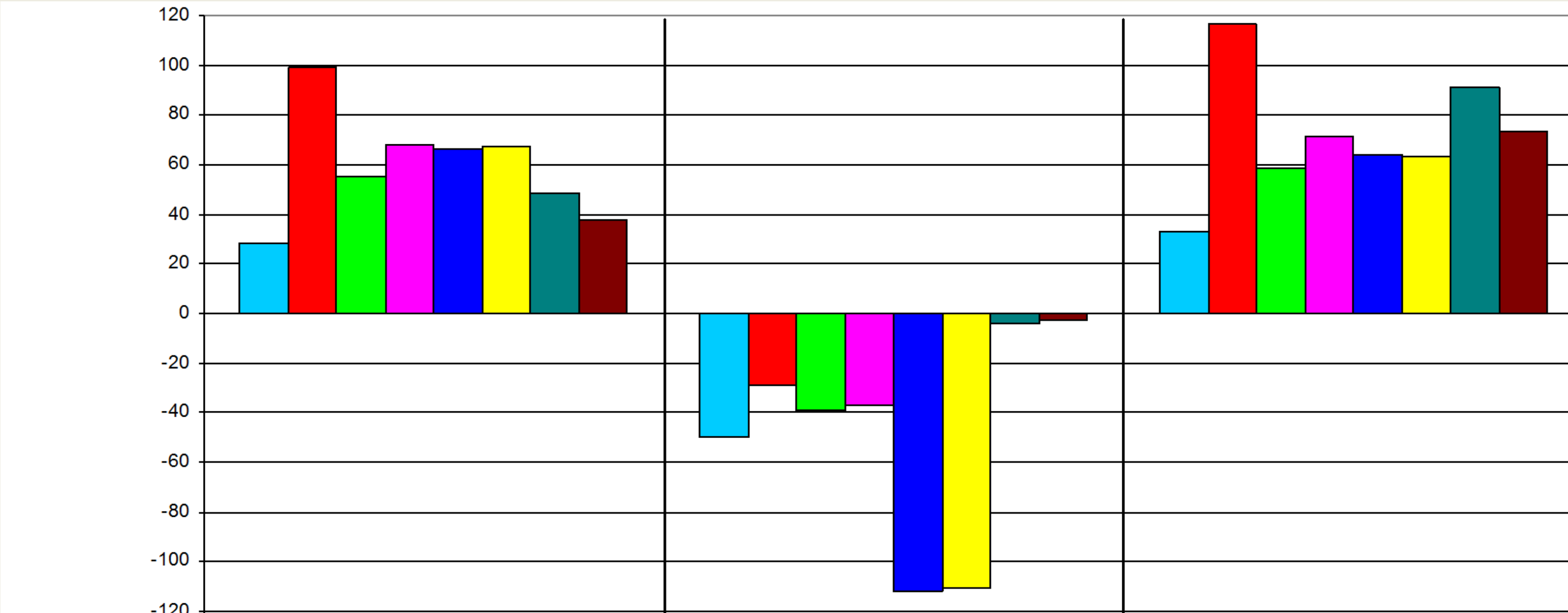



*Figure 3. The chromaticity **x-y** diagram of the sample luminescence*

# Outcomes of the analysis: CIE L*a* b*

- Colouristic distribution was measured by the Lab system.
- Results obtained from the previous measurements (Fig. 2 and Fig.3) were confirmed on the the basis of the change diagrame of the CIE L * a * b * scale.
- Samples for luminescence colour coordinates without protective coatings and their changes using the PC 50 μm coating are displayed in Fig.4.




| | L* | a* | b* |
|---|---|---|---|
| 254 nm, 1 sl. PC | 28,6 | -49,9 | 33,1 |
| 254 nm, be dangos | 99,3 | -29,1 | 116,7 |
| 312 nm, 1 sl. PC | 55,3 | -39,3 | 58,5 |
| 312 nm, be dangos | 68,3 | -37 | 71,3 |
| 365 nm, 1 sl. PC | 66,1 | -111,7 | 63,9 |
| 365 nm, be dangos | 67,7 | -110,6 | 63,3 |
| 980 nm, 1 sl. PC | 48,4 | -3,9 | 91,1 |
| 980 nm. be dangos | 37,7 | -2,9 | 73,7 |

*Fig. 4. The diagram of the colour coordinate alteration in the CIE L*a*b* scale*

# Outcomes of the analysis: CIE L*a* b*

- The coordinate L (Fig. 4) shows the observed emission brightness (luminance) which is proportional to the observed intensity of the luminescence emission.

- Coordinates *a* and *b* express changes in colour of the observed image.

- As seen in Fig. 4, the PC coating suppresses the luminescence emission in the presence of the UV at 254 nm excitation wavelength.

- In this case, the total observed luminance of the colour/brightness decreases from 99.3 to 28.6 relative units.

- Moreover, the alteration and increased brightness in colour tone was observed. This evident from the coordinate point one in the x-y diagram with the PC coating and the point two without the coating.

# Outcomes of the analysis: CIE L*a* b*

- The lower change of the luminescence spectrum is observed when the wavelength of the UV 312 and 365 nm.

- It should be noted that the difference is closely correlated to the UV excitation wavelength.

- The intensity of the luminescence emission increases with the increasing wavelenght simultaneusly, it means that the image observed becomes visually brighter. Furthermore, the colour change is less significant.

# Outcomes of the analysis: CIE L*a* b*

- Analysing the impact of lamination in luminescence at excitation of 980 nm, it is evident that all different methods of measurement are significantly correlated, that is, they are similar in nature.

- It can be argued that the changes are minimal in regards to the emission rate at IR exposure (anti-Stokes luminescence) and the tone of the observed colour tone using a laminate coating.

- The same applies to the 365 nm UV exposure. It means that close UV range (254 and 312 nm) exposure for the luminescence excitation provides good results.

# Outcomes of the analysis: thermal effect

- Due to its thermal effect (temperature ranges from 90 to 110 °C) laminating technology as well as laminate coating may alter the luminescence characteristics.

- Polycarbonate (PC) is a commonly used material in the production of ID cards. Its glass transition temperature compared to the other polymers is sufficiently high  170–200 °C.

- Therefore, here we encounter the phenomenon which affects luminescence, i.e. thermal effect, as proved by the carried out experiments.

- The experiments were conducted based on the same methodology. The sample was heated by a controllable temperature source, and spectra were measured using the comporator VSC5000 (Fig. 5).

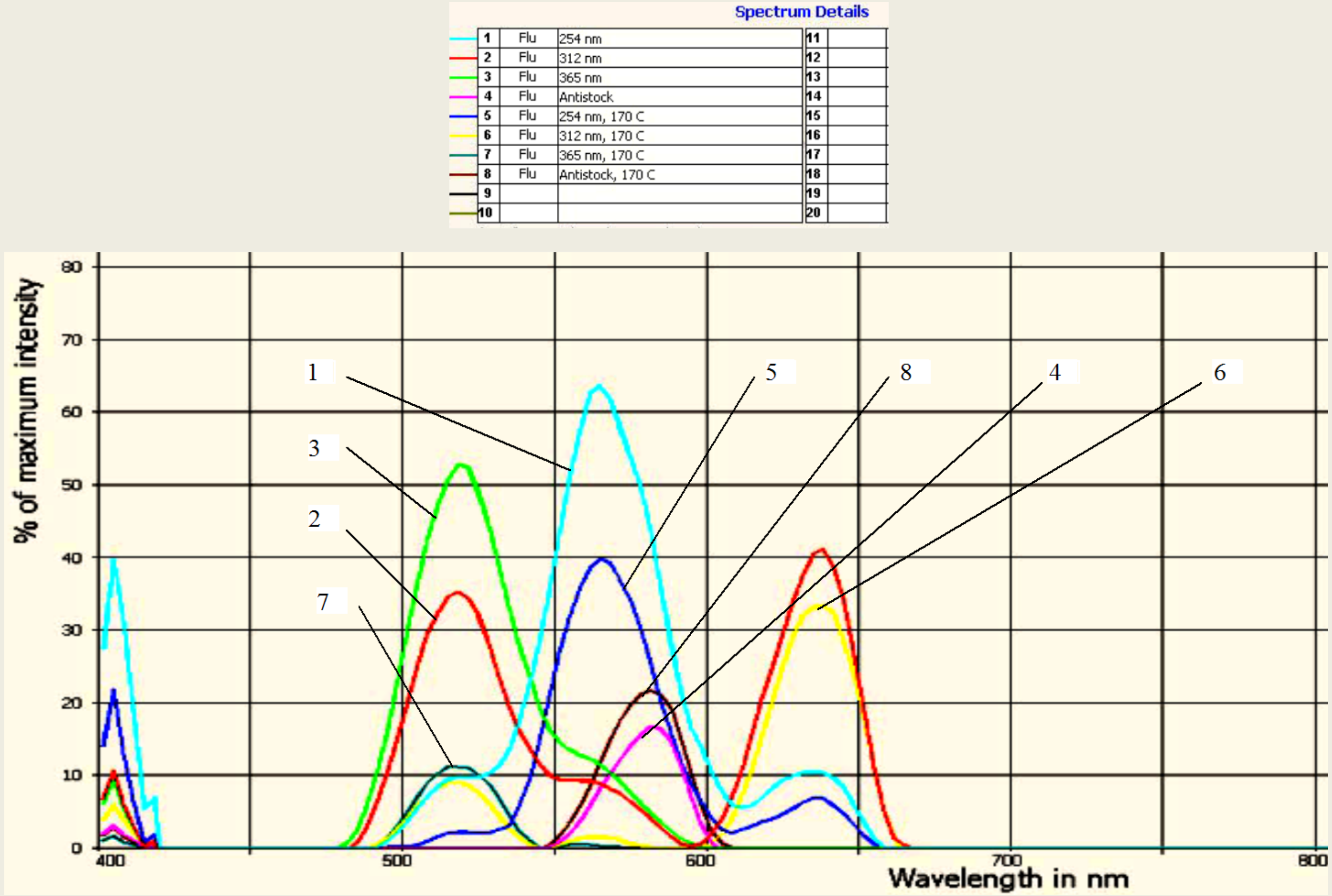



Figure 5. Spectrograms of the luminescence sample.
UV exposure under normal conditions – 245 nm (1), 313 nm (2), 365 nm (3).
IR exposure under normal conditions – 980 nm (4).
UV exposure after heating at 170 °C – 245 nm (5), 313 nm (6), 365 nm (7).
IR exposure after heating at 170 ºC – 980 nm (8)

# Outcomes of the analysis: thermal effect

- Heating enhances the luminescence effect. Increase in luminescence is proportional to the increase in temperature and is significant in the relative value.
- In addition, relaxation processes should be taken into consideration. It means that within a particular period, luminescence intensity may decrease.
- Coloristic properties/colour changes are provided in the chromaticity xy diagram.
- The colour coordinates without heating and after heating of the print up to 170 °C, at UV and IR luminescence exposure after excitation are presented in Fig. 6.

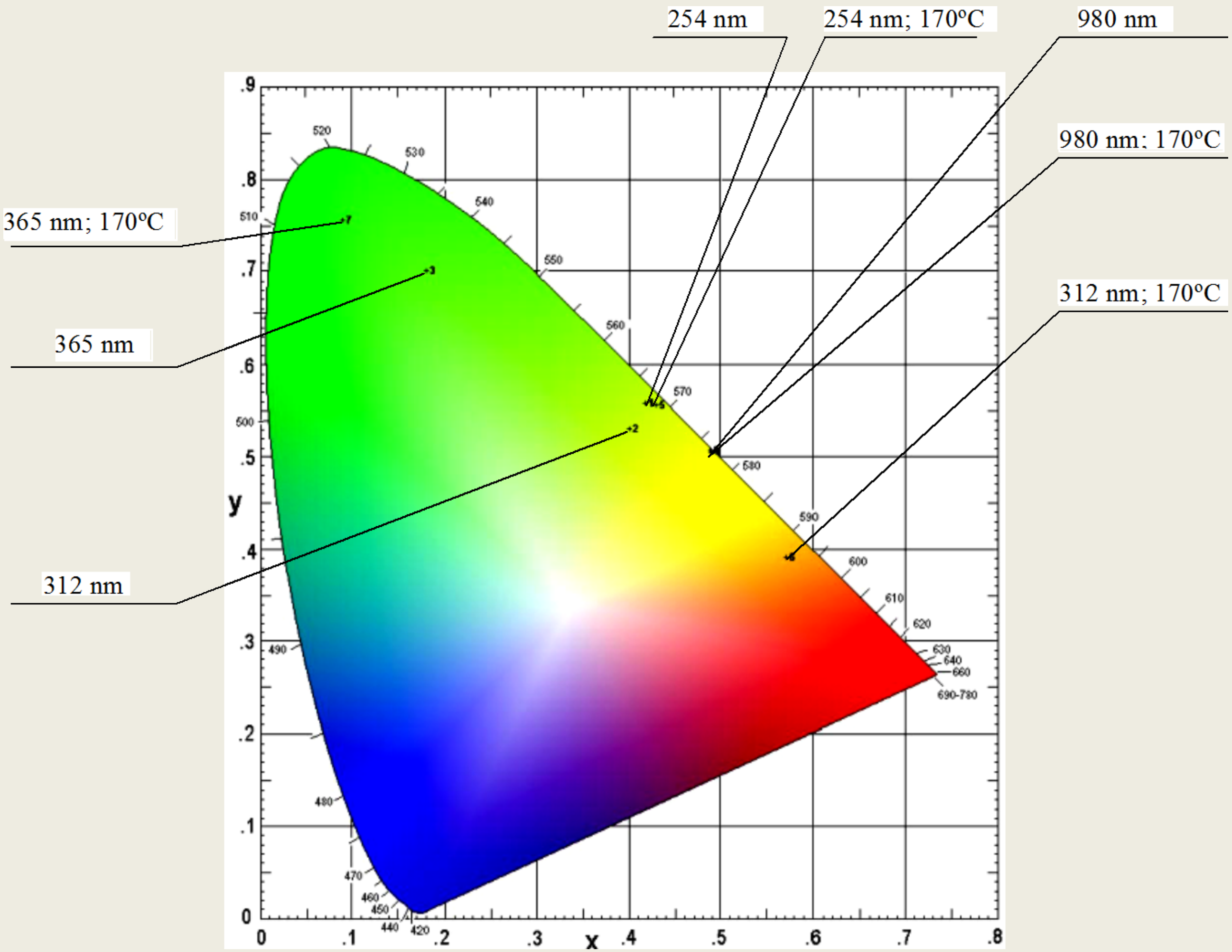



Figure 6. Chromaticity **x-y** diagram under normal conditions and after heating at 170 °C

# Outcomes of the analysis: thermal effect

- As seen in the diagram (Fig, 6), when excited by 312 nm UV exposure there were significant changes in the luminescence wavelenght/colour.
- The change depends on the temperature.
- When the print is heated to 170 °C, colour moves in the direction of longer wavelenght (red color).
- At 365 nm excitation, luminescence wavelenght slightly decreases.

# Outcomes of the analysis

- The obtained results suggest that the colouristic characteristics of luminescent inks may be contrary to the ones declared by the manufacturer.

- In order to fully assess the durability of inks and identification level, the long-term reliability of ultraviolet effects (solar radiation) and relative humidity should be determined.

- The laminate significantly reduces the luminescence at $\lambda$ = 254 and 312 nm excitation wavelenght exposure (81 % and 27 % respectively). Given such loss of luminescence energy, the product lamination becomes indesirable.

# Outcomes of the analysis

- When the heating temperature of the print is increased, luminescence emission significantly decreases.

- For example, at 170 °C the emission may be reduced to 37–77 %.
- Luminescence intensity decreases while increasing UV exposure / excitation wavelength.

- For example, after heating the print to 170 °C, excitation λ = 254 nm UV luminescence is reduced to 37 %, while at the UV excitation λ = 365 nm, luminescence intensity decreases to 77 %.

- For these reasons, hot lamination for the products with the luminescent inks QFX with the identifiable elements is not recommended.

# Thank You for attention

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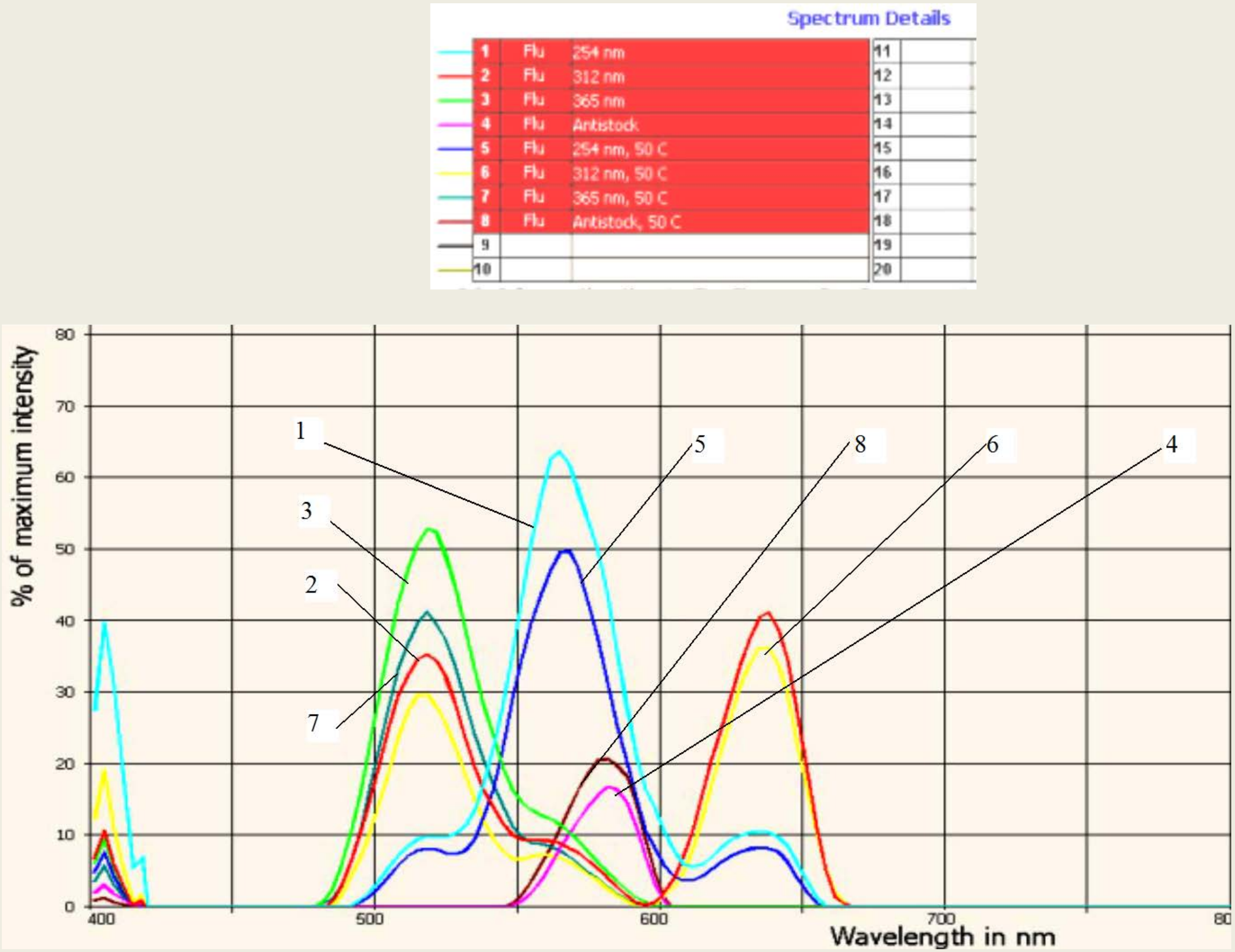
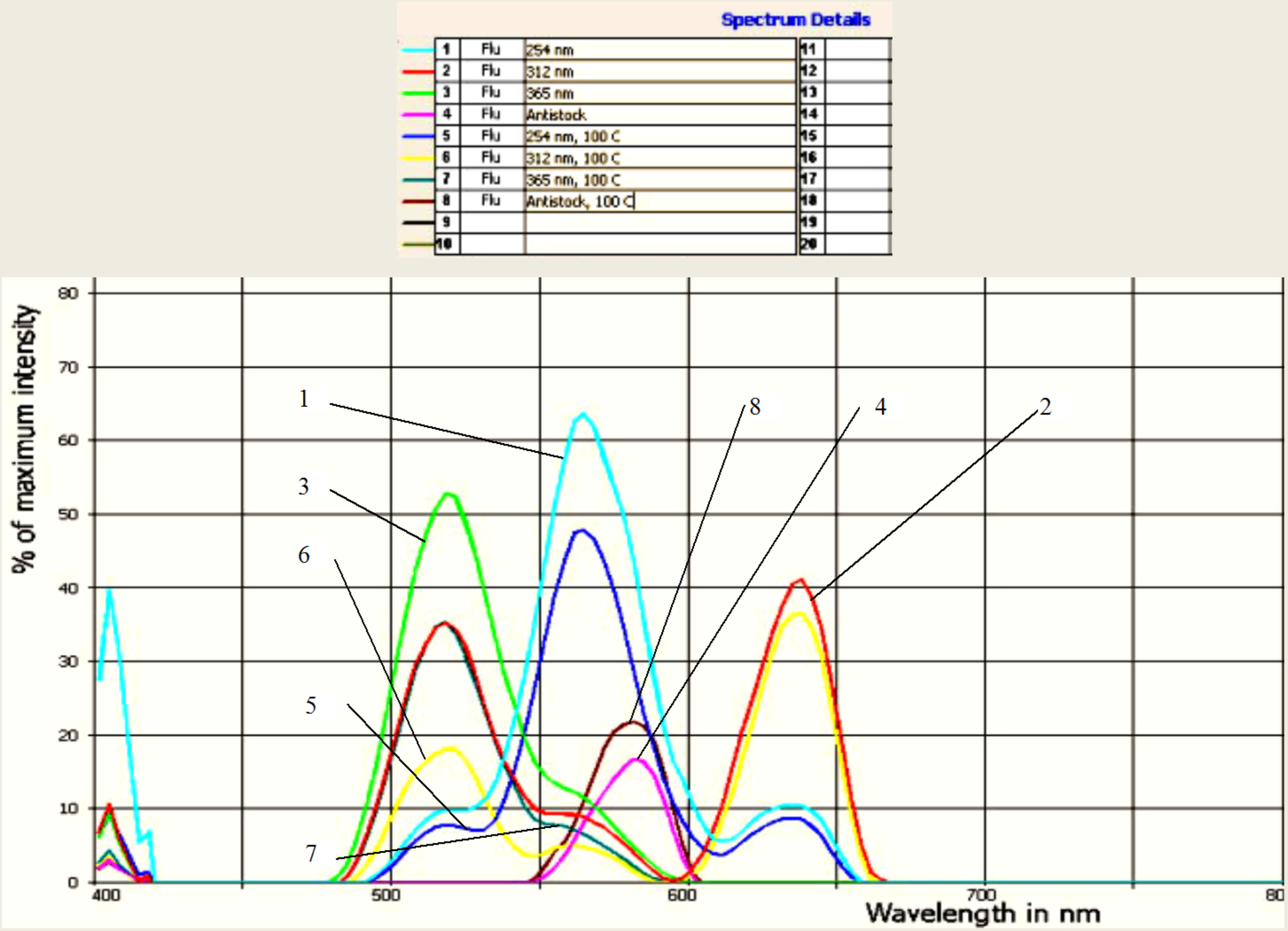
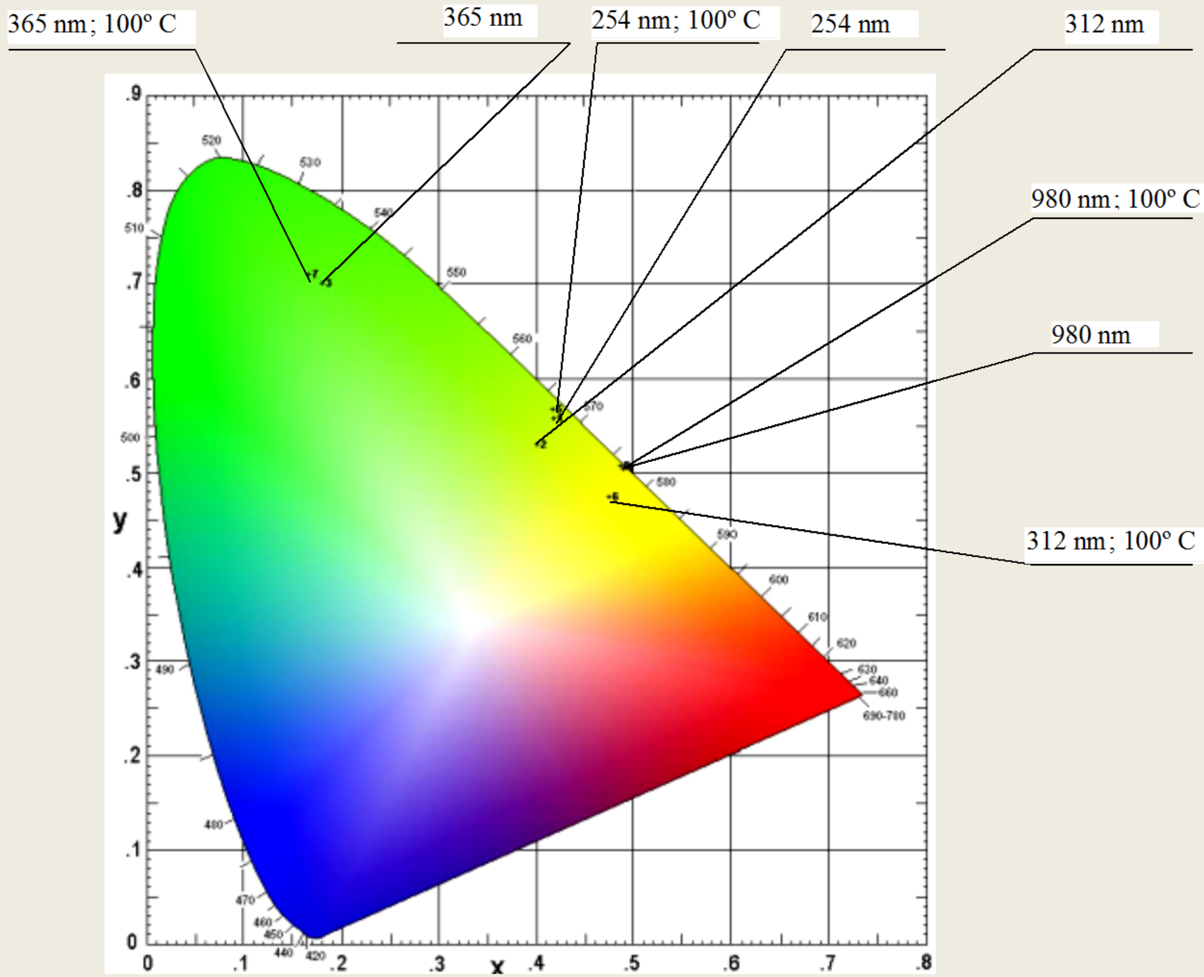
# Papildomai



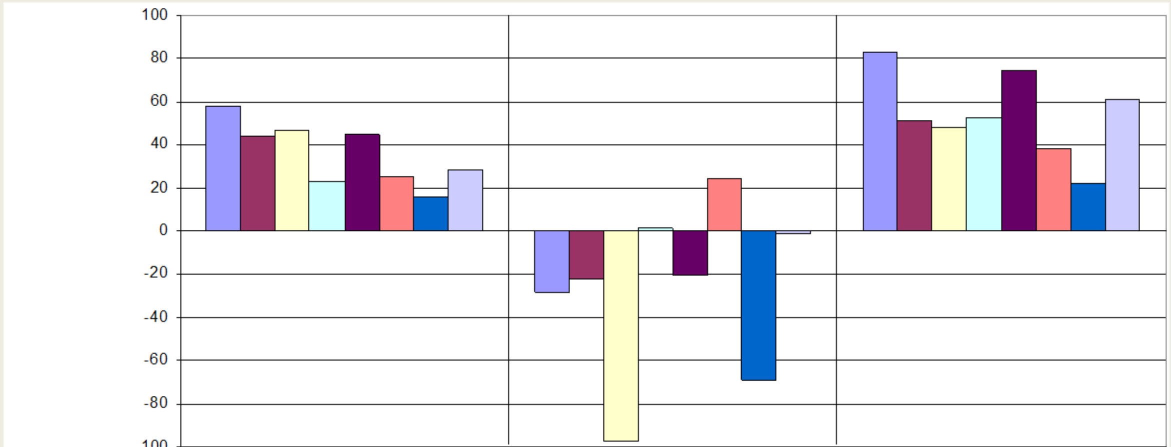

7 pav. Bandinio liuminiscencijos spektrogramos. UV apšvita normaliomis sąlygomis- 245 nm (1), 313 nm (2), 365 nm (3). IR apšvita normaliomis sąlygomis– 980 nm (4). UV apšvita po 50ºC kaitinimo-245 nm (5), 313 nm (6), 365 nm (7). IR apšvita po 50ºC kaitinimo-980 nm (8).




8 pav. Bandinio liuminiscencijos spektrogramos. UV apšvita normaliomis sąlygomis- 245 nm (1), 313 nm (2), 365 nm (3). IR apšvita normaliomis sąlygomis– 980 nm (4). UV apšvita po 100ºC kaitinimo-245 nm (5), 313 nm (6), 365 nm (7). IR apšvita po 100ºC kaitinimo-980 nm (8).




10 pav. Bandinio liuminescencijos koloristinės **x-y** diagramos normaliomis sąlygomis ir po 100ºC kaitinimo




| | L* | a* | b* |
|---|---|---|---|
| 254 nm | 57,8 | -28,2 | 83,1 |
| 312 nm | 43,8 | -22,1 | 51 |
| 365 nm | 46,7 | -97,6 | 48,3 |
| 980 nm | 23,3 | 1,1 | 52,7 |
| 254 nm; 170 laipsn. | 44,6 | -20,6 | 74,3 |
| 312 nm; 170 laipsn. | 24,8 | 24,4 | 38,4 |
| 365 nm; 170 laipsn. | 15,8 | -69,4 | 22,5 |
| 980 nm; 170 laiosn. | 28 | -1,5 | 61,4 |

12 pav. Liuminescencijos koloristinių koordinačių kaitos diagrama CIE L*a*b* sistemoje normaliomis sąlygomis ir po 170ºC kaitinimo