Raman spectroscopy for the control of soil contamination by copper ions

E.V. Timchenko¹, P.E. Timchenko¹, L.A. Zherdeva¹, N.V. Tregub¹, L.A. Shamina¹
¹Samara State Aerospace University (SSAU), 443086, Samara, Russia
E-Mail: laser-optics.timchenko@mail.ru

Abstract. The experimental results of changes in the plant optical characteristics depending on the concentration of copper ions in the soil were presented by a method of Raman spectroscopy. Raman spectral features of plant tissue growing under the influence of copper ions in the soil that exceed the MPC were obtained. The basic changes were registered at Raman bands 1325 cm⁻¹, 1527 cm⁻¹ and 1547 cm⁻¹ that responsible for the stretching vibrations of chlorophyll a and b, carotene and chlorophyll a. The optical coefficient based on the dependence of the copper ion concentration from the optical parameters of plants was introduced. When the concentration of copper ions in the soil of 3 MPC observed increase optical coefficient values on the first day of experiments.

1. Introduction
In today’s, environmental problems in their public importance left on one of the first places. The priority issue in ecology is to develop methods to control atmospheric emissions. Especially dangerous are the industrial enterprises, which are the sources of emissions of heavy metals, which have a negative impact on the entire ecosystem. One of the most common heavy metals emitted by enterprises is copper [1]. At concentrations of copper ions in the soil, it is much higher than the one of the MPC biotoxic heavy metals. However, the localization and accumulation of copper ions in the soil is not of a permanent nature, as it depends on the "wind rose". Considering that the plant leaves are the most sensitive to the action of atmospheric pollutants, plants can be used as "markers" environmental state of the atmosphere and their optical characteristics to serve as a quantitative measure of the environment. In order to control atmospheric emissions using physical and chemical methods of environmental monitoring, including optical [2] and chromatographic techniques [3]. Because of the specific characteristics of electrochemical and chromatographic methods require time-consuming and quite laborious. Optical methods are deprived of these drawbacks are not destructive analysis methods based on the relationship and the optical properties of the system and its composition. The most common methods include optical fluorescence analysis, the method of inverse scattering, absorption analysis, the method of Raman spectroscopy (RS) [4-7]. In the paper [8] describes the use of Raman spectroscopy to elucidate structural changes in plant tissues and individual cells under the influence of pollutants. In [9] the possibility of finding TiO2 using Raman spectroscopy. Therefore, Raman spectroscopy was selected as the basic method for the control the copper ions in the soil, which has high sensitivity and provides the most complete information about the state of a living system, in contrast to other optical methods.

2. Materials and methods of research
As the test is selected bioindicator copper peas (Pisum). We investigated the following groups of
plants that are in the same environmental conditions (light and humidity) control samples, samples of plants grown in soil with different concentrations of copper ions in the soil 0.2MPC, 0.5MPC, 1MPC, 2MPC, 3MPC. The concentration of copper ions was entered once before the start of the experiment. Raman spectroscopy method has been implemented with the help of experimental stand shown in Figure 1.

![Experimental setup](image)

**Figure 1.** Experimental setup: 1 - the object; 2 - Raman Probe RPB785; 3 - Laser Module LuxxMaster Raman Boxx; 4 - power supply of the laser module; 5 - spectrometer Shamrock sr-303i; 6 - Built-in cooling chamber DV420A-OE; 7 - the computer; 8, 9, 10 - information electric cables; 11 - transmitting fiber; 12 - the receiving fiber

Processing Raman spectra was carried out in a software environment Mathematica'8. To suppress background fluorescence and Raman spectra allocation method was used polynomial approximation. The result of the test experiments, it was found that the error factor used is 7%.

### 3. Research results

Figure 2 shows a typical Raman spectrum of the test plants. The following Table 1 provides a breakdown of the main bands of Raman spectrum.

![Raman spectrum](image)

**Figure 2.** The intensity of the Raman wavenumbers for the selected bioindicator.

**Table 1.** Explanation of the main bands of Raman spectrum.

| Wavenumber , cm⁻¹ | Component       |
|-------------------|-----------------|
| 740               | Chlorophyll a and b |
| 915               | D - glucose     |
| 1110              | D - glucose     |
As seen in Figure 1, the main optical changes of plants grown in the presence of copper ions in the soil is 1325 cm\(^{-1}\), 1527 cm\(^{-1}\) and 1547 cm\(^{-1}\), responsible for the stretching vibrations in chlorophyll a and b, carotene and chlorophyll a. However, it is known that the change of chlorophyll concentration "a" in the plant leaves is informative factor of environmental influences on the plant [10, 11], which in turn is reflected in the intensity of the RS. As can be seen from Fig. 1 Raman band at 1547 cm\(^{-1}\), corresponding to stretching vibrations of chlorophyll "a" clearly expressed for the plants grown under the influence of copper ions with a concentration 3MPC.

As it has been shown in [12] a relatively constant parameters considered lignin in plants. The deposition of lignin in the cell walls increases their strength. Thus, the ratio of the intensity of the Kyrgyz Republic, proportional to the concentration of chlorophyll "a" and carotenoids to the intensity of the Kyrgyz Republic, proportional to the concentration of lignin, reflect, including changes in the concentration of pollutants and can serve as an indicator of the effect of hydrogen on plants. Thus, it was introduced the following optical coefficient R, which allows to determine the effect of copper on the plant:

\[
R = \frac{I_{1527}}{I_{1547}} \frac{I_{1547}}{I_{1600}}
\]

where \(I_{1527}\) – Raman intensity on the wavenumber 1527 cm\(^{-1}\), which is proportional to C = C stretching vibrations in the b-carotene in the leaves of plants; \(I_{1547}\) - the intensity of Raman for the wave number 1547 cm\(^{-1}\), which is proportional to the concentration of chlorophyll in the leaves of plants; \(I_{1600}\) - the intensity of Raman for the wave number 1600 cm\(^{-1}\), proportional to the concentration of lignin in the plant leaves.

Further, Figure 3 shows the dependence of optical coefficient values plants grown in soils with different concentration of copper ions of time.

**Figure 3.** The dependence of the optical coefficient for soils with different concentrations of heavy metals on the time.
Figure 3 shows that the optical coefficient values (R) for plants grown in soil at a concentration of copper ions 3MPC higher than the values for R 1MPC. While in the last days of the life cycle of the plant occurs reverse pattern, which is probably due to the fact that the greatest concentration of copper ions in the soil causes the acceleration of the life cycle of plants, resulting in degradation of the major pigments in plants, which in turn affects the optical parameters change plants. Further, Figure 4 shows the dependence of optical coefficient values plants concentration of copper ions.

![Figure 4. The dependence of the optical coefficient on the concentration of copper in the soil.](image)

Figure 4 shows that the concentration of copper ions in the soil equal to 3 MPC, an increase in the values of the optical coefficient in the first days of the experiment, indicating that the nature of the impact volley of copper ions in the plant.

4. Conclusion
Was particularly the Raman spectrum of plants growing under the influence of copper ions in the soil exceeding the MPC. Basic changes were registered in the wave numbers 1325 cm$^{-1}$, 1527 cm$^{-1}$ and 1547 cm$^{-1}$, responsible for the stretching vibrations in chlorophyll a and b, carotene and chlorophyll a.

Was introduced optical coefficient on the basis of which the dependence of the concentration of copper ions from the optical parameters of the plants. When the concentration of copper ions in the soil of 3 MPC observed increase optical coefficient values on the first day of experiments.

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