

To the study of products of honey bee *Apis mellifera* L. Caucasica

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ABSTRACT

Results of detection of photosensitivity of propolis of a honey bee- *Apis mellifera caucasica* widespread in Azerbaijan are presented in article. During studying optical and electric properties of propolis the photoluminescence with a radiation maximum is revealed with a length of wave of 430 nanometers

Method of atom-absorbing spectrometry on AAC 300 Perkin Elmer it is established that with increase in distance from sources of anthropogenic emissions, concentration of metals in apitoxin, propolis and pollen considerably decreases and corresponds: Fe (1.15), Mn (5.1), Cu (0.24), Zn (4.7), Cr (0.02) mg/kg in Shemakhi and Fe (1.16), Mn (5.2), Cu (0.26), Zn (5.1), Cr (0.03) mg/kg in Sumgait accordingly.

In samples of bee products collected in Sumgait and Shamakhi, revealed activity of radionuclides in the γ -spectrometers "Canberra" detector HP Ge. Installed, the activity of radionuclides K^{40} , Ra^{226} , Th^{232} , Cs^{137} , U^{235} , U^{238} in samples of products of honeybees *Apis MELLIFERA* L. *Caucasica*.

Possibility of preparation of photosensitive detectors on the basis of natural biologically active agents p-InSe-p (propolis) where propolis behaves as the semiconductor of r-type of conductivity is revealed and proved.

KEYWORDS: *Apis mellifera* L. *caucasica*, radionuclide, propolis, heterocontact, metals

INTRODUCTION

Chemical and pharmacological properties of biologically active substances of insects under the influence of ecological factors strongly vary. In Azerbaijan widespread melliferous bee is *Apis mellifera* L. *Caucasica*. Products of its vital activity are – bee sting, wax, honey, a uterine milk, propolis, ambrosia, pollen.

All growing interest to apitherapy promotes the scientific approach to application of beekeeping products having great value in preservation of health of the person, and also to deeper studying of physical and chemical properties of products vital activity of bees and beekeepings.

Since ancient times honey bees are used by human for receiving honey, propolis, poison and other products of beekeeping.

Bees - best pollinators of crops and other plants. The composition of bee venom enzymes include – fosfolipaza A₂, hyaluronidase, phosphatase, alpha-glucosidase, beta-galactosidase; toxic polypeptides – melittin, apamin, MCD-peptide tertiapine, secapine; biogenyamin - serotonin, histamine, catecholamines. The chemical composition of venom varies with age of bee [1, 2, 3,4].

The data on the research of apotoxin is cited in the literature, however many questions still remain not mentioned and demand the deep analysis and studying [5].

One of the most significant and extended in the world natural medical and prophylactics means are beekeeping products - honey, propolis, a uterine milk, pollen, wax, the bee sting possessing high physiological activity, and also ubiquity of dwelling of bees and relative simplicity of their reception. The melliferous bee is an insect what is exclusively well adapted for a role of the indicator of environmental contamination, because life of bees is closely connected with habitat [6].

Range of organic compounds used in micro-and optoelectronics, continuously expands. In the process of making various types of optoelectronic devices biologically active substances of both animal and vegetable origin are involved It was revealed that despite the chemical

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interaction between the semiconductor substrate and the components of organic matter, molecular structural ordering of propolis films is the same for films of this material obtained on the surface of amorphous glass substrates. Propolis used in the pharmaceutical and cosmetic industry porfyumerno is a complex mixture of organic compounds consisting of 50-55% of resinous substances, wax up to 30%, and 10% of essential oils and balms. The composition of propolis includes organic acids, antibiotics, vitamins, trace elements (Al, V, Fe, Ca, Si, Mn, Sr), and from natural enzymes – carotene. It was revealed that as a result of chemical and deformation interaction between organic matter and the formation of a layered compound is an organic-inorganic nanoscale sandwich structure at a distance of $\sim 0.3\mu\text{m}$ from the interface layered crystal-propolis [7].

In this paper the authors showed the principal possibility of manufacturing a semiconductor photosensitive structures, a waste product of bees propolis. The authors noted that the electric properties and photosensitivity range of structures depends on the aggregate state of the organic matter (liquid, solid), its mode of application to a semiconductor wafer and the substrate material. In addition, heterocontacts in a semiconductor-propolis have significant photosensitivity [8].

From the above it follows that despite minor literary data on the study of bee products, many questions still remain unaffected and require in-depth analysis and study [9,10,11].

The effect of temperature on the electrical parameters of metabolic products of the honeybee *Apis mellifera* L. caucasica, widespread on the territory of Azerbaijan was not studied. Based on the above, the study of electrophysical parameters of bee products to investigate the photo-thermal stability and their seemed to be relevant.

The aim of our research - identifying electrical properties of propolis honeybee *Apis mellifera* L. *Caucasica*, collected from bees in apiaries with relatively cleaner territories of Azerbaijan, as well as identifying the impact of environmental pollutants and radiation on the chemical composition of the venom.

MATERIALS AND METHODS

The chemical composition of propolis collected in apiaries bees that are in the vicinity of Shamakhi and Sumgait showed variability in the quantitative composition of the chemical elements.

The elementary structure of propolis of melliferous bee *Apis mellifera* L. *Caucasica* has been studied by the method of atom-absorbing spectrometry on AAC 300 Perkin Elmer. The variability of their elementary structure, received from bees, from various ecosystems of Azerbaijan has been defined. It is established that with increase in distance from sources of anthropogenic emissions, concentration of metals in apitoxin, propolis and pollen considerably decreases and corresponds: Fe (1.15), Mn (5.1), Cu (0.24), Zn (4.7), Cr (0.02) mg/kg in Shemakhi and Fe (1.16), Mn (5.2), Cu (0.26), Zn (5.1), Cr (0.03) mg/kg in Sumgait accordingly.

Determination activity of the radionuclide's in the products of ability to live of bee *Apis mellifera* L. *Caucasica* as, was specified at "Canberra" γ -spectrometer with a plenary Ge-detector.

Activities of uranium isotopes are determined according to the following peaks on gamma-spectrometer. Activity of ^{235}U was determined according to gamma peak with 185.7 keV energy and 54, and activity of ^{238}U isotope according to gamma peak with 1001.03 keV energy and 0.59% yield of metastable $^{234\text{m}}\text{Pa}$ isotope, which is its daughter nucleus. It should be mentioned that activity of ^{238}U isotope in the solution before sorption can be determined on gamma-spectrometer.

Radiation activity of elements in samples of products of ability to live of melliferous bee *Apis mellifera* L. *Caucasica* collected in the Sumgait and Shamakhi of Azerbaijan on fig.1 „Canberra“ γ -spectrometers with HP Ge detector. It was determined the activity of radionuclide's radionuclides (^{40}K , ^{226}Ra , ^{232}Th , ^{137}Cs , ^{235}U , ^{238}U) in the samples of products of ability to live of melliferous bee *Apis mellifera* L. *Caucasica* (fig.1).

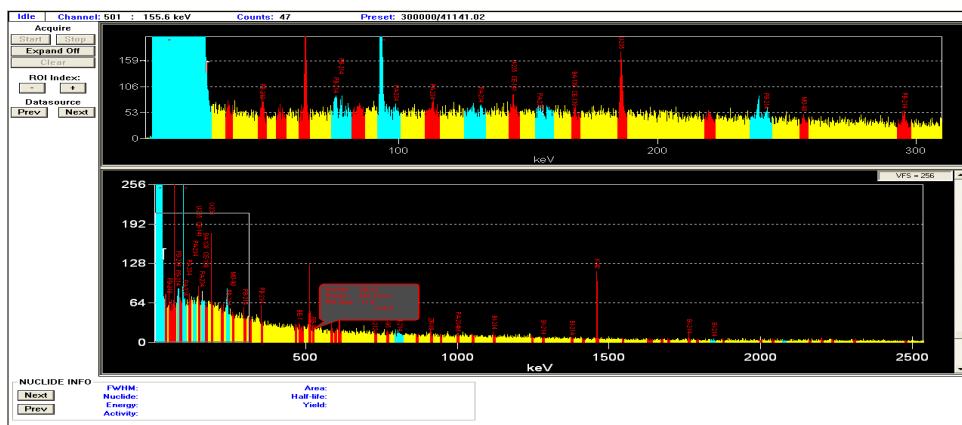


Fig.1. Spectra of radionuclide's in samples of products of ability to live of melliferous bee *Apis mellifera* L. Caucasia.

Therefore, for our research we took propolis collected by bees located on apiaries near Shamakhi.

Firstly for Research on electrical and optical properties of propolis were prepared honeybee propolis thin films deposited on a metal substrate by us.

Studies of the temperature dependence of the resistivity ρ for propolis was conducted. For that an alcoholic solution of propolis on a metal substrate coated with silver paste. On the other surface of the metal substrate electrode of silver paste was stuck. To form nanoscale sandwich structure, 96% alcoholic solution of propolis was prepared. This solution was applied to a metal substrate and placed in a centrifuge for a uniform distribution over the surface. As a result, during centrifugation and evaporation of the alcohol nanoscale thin film of propolis was prepared.

In order to investigate the electrophysical parameters of propolis, heating of sample was performed in the measuring cell at a constant rate $9,1^\circ \text{C} / \text{sec}$. Resistance measurement was performed by teraohmmetr E6-13A.

Propolis samples was gradually heated and change in resistivity was observed. Photosensitivity propolis was studied by measuring the photoconductivity in the wavelength region 0.2mkm 2microns .

The curves of the resistivity ρ of the sample heating temperature: $\rho = f(T)$ are presented in Figure 2.

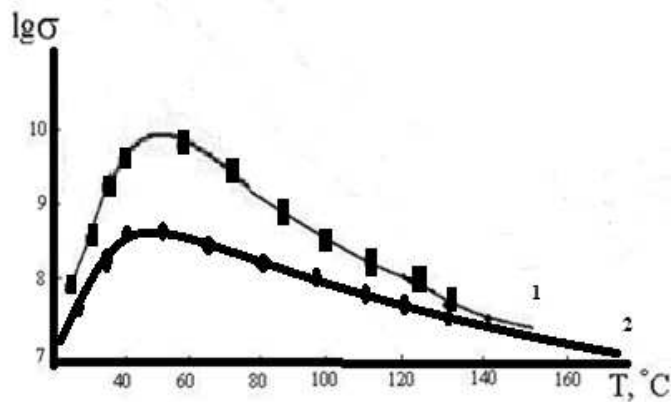


Fig.2. Schedule dependence of the resistivity ρ of the heating temperature of the sample: $\rho = f(T)$.

As can be seen from Figure 1, when the temperature is increased there was a gradual increase in heat resistivity (curve 1). When heated to a temperature of propolis samples 150 ° C, the change of the resistivity of samples of propolis was noted. From the results of the research it is clear that, the effect of heating temperature on the structural changes, in turn has a direct impact on the change in the pharmacological activity of propolis.

When re-heating the samples of propolis, noted the change (decrease) in resistivity (curve 2). We assume that after heating a sample of each structural changes occur, which in turn causes a decrease in the resistivity of the samples propolis.

From the data obtained resistivity of propolis can be stated that propolis samples in the temperature range between 50 ° C behave as semiconductors. In semiconductors, the temperature dependence of the resistivity and conductivity for a certain range of temperatures is determined by the dependence of the form:

$$\rho = \rho_0 e^{\beta/T} \quad (1.1);$$

$$\sigma = \sigma_0 e^{-\beta/T} \quad (1.2);$$

where ρ_0 , σ_0 , β - constants for a given temperature range and characteristic of the propolis.

Based on the results of the research it can be seen that under the influence of temperature on samples of propolis change in resistivity is marked.

On the basis of the experimental data propolis conductivity depending on the temperature is defined by us. The curve of the conductivity σ of a sample heating temperature $\sigma = f(T)$ in time were created.

It should be noted that under the influence of temperature change in the electrophysical parameters of propolis is marked.

Identified changes in resistivity (conductivity) of propolis, is likely resulted from changes in electrical properties of propolis.

Measurement of absorption spectra of test samples apitoxins UV-visible region was conducted on the UV-VIS spectrometer Specord 250 PIUS - 223G 1020 at a wavelength of 320 nm and the rate of 5 nm/sec in the wavelength range 180nm-1000nm.

In the samples of bee venom revealed two absorption maxima in the regions 206-212 and 220 nm due to the peptide bond and a weak absorption band in the range 265-280 nm, characteristic of aromatic amino acids.

Thus, the electrical properties of honey bee propolis was identified. Our data can be used for storage of honeybee propolis, as well as drugs based on it. We first defined the basic electrical and optical parameters propolis films. The transmission spectra of propolis was marked in the wavelength range from 180-1000 nm. Electrical conductivity at room temperature of propolis was defined. Simultaneously experimental studies to determine the temperature dependence of the electrical conductivity of propolis was conducted.

From the above it follows that the conductivity of the poison increases with temperature heating samples of propolis to 50°C. However, with a subsequent increase in temperature change in conductivity is observed, which means there is a decrease of conductivity.

Thus electrical and optical parameters of propolis films was defined. Conductivity was determined at room temperature and its temperature dependence was set. Transmission spectrum of propolis was measured at wavelengths in the range 180-1000 nm.

The studies conductivity and optical properties of honeybee propolis indicate that propolis is a semiconductor with an optical band width banned 3 eV. Thus propolis can be used in the development of various optical devices, including photodetectors.

Findings

As a result of experimental studies of the electrophysical properties of propolis, photoluminescence of propolis films was revealed at room temperature.

Maksimum propolis photoluminescence films at room temperature is observed at a wavelength of 430 nm.

Method of atom-absorbing spectrometry it is established that with increase in distance from sources of anthropogenic emissions, concentration of metals in apitoxin, propolis and pollen considerably decreases and corresponds: Fe (1.15), Mn (5.1), Cu (0.24), Zn (4.7), Cr (0.02) mg/kg in Shemakhi and Fe (1.16), Mn (5.2), Cu (0.26), Zn (5.1), Cr (0.03) mg/kg in Sumgait accordingly.

Heterojunction monoselenide propolis and indium p-InSe-p was created.

The possibility of the preparation of photosensitive detectors based on natural biologically active substance propolis and monoselenide indium - p-InSe-p was noted ..

It was revealed that propolis biosensors behaves like a semiconductor p-type conductivity.

In samples of products of honey bees *Apis MELLIFERA* L. *Caucasica* installed the activity of radionuclides K^{40} , Ra^{226} , Th^{232} , Cs^{137} , U^{235} , U^{238} .

REFERENCES

1. <http://medportal.ru/enc/nutrition/therapy/7/>
2. http://www.chemistry-chemists.com.N2_2013.S1.t3.htm
3. <http://www.bibliotekar.ru.med.med.16-3.htm>
4. Antunez, K., J. Harriet, L. Gende, M. Maggi, M. Eguaras, P. Zunino, 2008, Efficacy of natural propolis extract in the control of American foulbrood. *Vet. Microbiol.* (131): 324-331.
5. Krylov V. N Apitoxin - what is it /Beekeeping, 1993, № 2. – P.36-39.
6. Jedryszek A. Bees and products beekeeping as an indicator of soiling a surroundings // *Med. Weter.* 1987. V.43, N 6. P. 352-356.
7. Drapak OI Gavrilouk SV, Kaminsky VM, Kovalyuk ZD, 2008, X-ray studies of molecular propolis films formed from the alcohol solution on the cleaved surface of layered compounds A25 B3 6. *Journal of Technical Physics, Ukraine.*78(9): 112-119.
8. Drapak OI Drapak ID, Kovalyuk ZD, 2004, Optical and electrical properties of propolis films. *Journal of Technical Physics, Ukraine.* 74(11): 136-137.
9. Sh.A Topchiyeva.S.A. Huseynova, A.M.Mageramov, 2004, Influence of small doses γ -radiations on molecular mobility, spectral characteristics and pharmacological properties of poison of melliferous bee –*Apis mellifera caucasica*. 40th IUPOC International Symposium on Macromol, WORLD POLYMER CONGRESS MACRO, Paris-France. (5.3.): 119.
10. Mamedova F.Z, Topchieva Sh.A.. 2012, Effect of gamma radiation on the waste products of honeybees (*Apis mellifera* L, *Caucasica*). *Journal Bulletin of Zaporizhzhya National University, Biological Sciences, Zaporozhye*, (3): 66-71.
11. Topchiyeva Sh.A., Mammadova F.Z., Yusifov R.Y., 2011, The influence of environmental factors (heavy metals) on the chemical composition of the venom of the honeybee *Apis Mellifera* K. The articles of Institute of Zoology Azerbaijan National Academy of Sciences (XXIX): 469-473.