



APPLICATION OF INFRARED SEMICONDUCTORS INTERFERENCE FILTERS FOR OPTICAL SENSORS IN EXPRESS SPECTROSCOPY OF ORGANIC MATERIALS

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Abstract: *The presence in food and the environment of nitrates, organic and other substances harmful to humans can be identified by their characteristic molecular spectra in the near infrared radiation. When developing optical sensors, whose work is based on the determination of the spectral absorption characteristics of organic matter, it is necessary to apply cutting optical filters for the selection of certain infrared ranges of the spectrum. The work carried out to develop multilayer thin film interference filters with replaceable cutting position limits infrared radiation depending on the concentration and type of the studied compounds. The peculiarity of these filters is the use of semiconductor crystals In_4Se_3 , In_4Te_3 and $CdSb$ as substrates for thin-film multilayer coating. High stability of the spectral characteristics, resistance to chemicals and atmospheric action of single crystals In_4Se_3 , In_4Te_3 and $CdSb$ enables the design based on these filters with $\lambda=1,7-6,5$ μm different positions of shortwave radiation limits cutting range and a maximum transmittance $T_{max}=91-95\%$. The method of SEM studies depending on the structure of thin films - component filters ZnS , SiO , Ge , Te , SrF_2 on technological factors and on spectral and mechanical stability of the multilayer coating are used. The requirements to design solutions of the active cell optical biosensor developed with the use of infrared filters. The method and simulation modeling to build adaptive reconfigurable computer information-measuring system of rapid analysis of qualitative composition and quantitative parameters of molecular spectra of bioactive substances are proposed.*

Keywords: *optical sensor, multilayer thin films, interference filter, adaptive reconfigurable computer information-measuring system*

1. Introduction

In developing biosensors use of organic complexes and materials change their electrical or optical properties under the influence of external physical factors (temperature, electromagnetic radiation, mechanical stress, etc.), or when they are surface or bulk chemical interaction with other chemicals elements and complexes in aerate or liquid phase [1-3]. Feature of

optical biosensors are subject to change spectral characteristics of reflection or transmission of electromagnetic radiation sensitive layer of the sensor as in the visible, i.e. the optical and ultraviolet (UV) and infrared (IR) spectral region [4, 5]. IR spectroscopy in comparison with UV and visible range into wider use in biotechnology, medicine, pharmacology studies for quantitative and qualitative composition of substances on the content

of amino acids, proteins, bacteria, inorganic compounds and other constituents analysis [6]. This is due to greater information content of IR spectra concerning the molecular structure of matter. In addition, a high-energy radiation shortwave visible and UV range when irradiated with certain organic components can stimulate photochemical processes and lead to the destruction of the sensitive layer of the biosensor. Certain restrictions imposed on the permissible level of background effects of radiation nearby areas infrared wavelengths measured in information signals.

To improve the resolution IR method and the exclusion of undesirable constituents spectrum in the middle infrared region advisable to use in the optical path of the measuring channel thin-film multilayer interference filters that are applied to the respective semiconductor crystals. In the development of optical biosensors, whose work is based on the determination of the spectral absorption characteristics of organic matter, there is a need to apply cutting optical filters for selecting specific ranges of infrared spectrum. It is possible to distinguish two modes of investigation of the spectra of biosensor materials: 1) measurement and analysis of spectra own sensing elements; 2) measurement and analysis of changes in the spectra sensitive elements in their interaction with other monitored substances. Unlike biosensors with electrical conversion information where the sensor element must have a galvanic connection with semiconductor radiation detectors, may be by the part of the structure of the detector in optical biosensors or can confine the optical channel between the sensing element and the detector.

For example in [7] presented data from a study using human urine absorption infrared spectroscopy, which allows the characteristic absorption bands to

determine the qualitative characteristics of bioliquids in general. The authors used the method of sample preparation means "dried drop". With the contrasting observations in the spectrum of urea revealed characteristic bands with peaks in 3440, 3345, 3261, 1680, 1605, 1464, 1155, 1056 cm^{-1} and 557 cm^{-1} , corresponding to the wavelength range from 2.5 to 18 microns. The obtained experimental results are typical for stretching and deformation vibrations of complexes $(\text{NH}_2)_2\text{-CO}$ and their derivatives. The observed shift of the position of the maxima on the value of 10-20 cm^{-1} in the absorption spectra of the authors explain the different options for different pathology specimens that own properties biomaterial. But apparently similar changes may be characteristic spectra and the results of the interaction of urea with outside groups -CO .

For other biosensitive materials [8] may be important changes in their spectra due to their natural aging. We believe this underlines the importance of dynamic updating databases spectra used biosensors and periodic calibration of measuring paths of control devices during their operation. This approach will improve the resolution of information-measuring system for improved detection and differentiation of the components of the studied mixtures. Increasing contrast investigated spectra can be achieved as the use of high contrast optical IR filter that would cut light noise (interference) in a given wave bands. Therefore, this work is dedicated to designing and testing new interference-absorption filters for short and medium infrared region, according to the measurement of the spectra of various organic liquids and create models of hardware and software reconfigurable specialized computer system for solving control problems tract spectrometer and measuring information processing in real-time.

2. Experimental

The feature of cutting off IR filters, which were developed in this paper are used as substrates for thin film multilayer coating of semiconductor crystals In_4Se_3 and In_4Te_3 [9]. The fundamental absorption is caused by an appropriate of band gap (0,65 eV for In_4Se_3 and 0,48 eV for In_4Te_3), and provides absorption component functioning filter. As substrates for filters used In_4Se_3 single crystals and In_4Te_3 , grown by the Czochralski method using Pelt'ye effect of which was pinned on cleavage plane of the plate thickness of 0,6–0,8 mm. High quality spectral characteristics, stability, resistance to chemical agents and atmosphere monocrystals In_4Se_3 , In_4Te_3 enable design based on these filters with different placement of short-cut boundary radiation in the range $\lambda_b = 1,7\text{--}7$ μm and maximum transmittance $T_{\max} = 91\%\text{--}95\%$. Applied to the surface of the crystals In_4Se_3 thin film and the In_4Te_3 antireflection and multilayer filter coatings can be made efficient cutting and bandpass filters for applications in optical devices [10, 11].

Calculation of thin-film interference structures of crystals for application to In_4Se_3 , In_4Te_3 and $\text{In}_4(\text{Se}_3)_{(1-x)}(\text{Te}_3)_x$ conducted standard matrix method of equivalent layers in combination with the method of smoothing the spectral characteristics in relation to the function that simulates the appearance of a given filter.

Cadmium antimony have similar to indium telluride crystals in the electronic properties and also can be used for IR signal filtering [10]. In addition, the use of indium selenide and telluride as their basis for photo-sensitive hetero structure has advantages [12, 13]. This allows combine constructively semiconductor filters and detectors in one device.

The developed software allows calculate

the spectral properties of multilayer interference coatings and analyze spectra reflectance and transmittance coatings for different values of the number of layers and their thicknesses and refractive indices. The input data of the program are the refractive indices of the individual layers n_j ($j=1\dots m$, where m - number of layers in the system), their optical thickness $d_j=n_j l_j$, where l_j - geometric layer thickness, and refractive index of the medium n_0 and the substrate n_s .

3. Results and discussion

The corresponding spectral characteristics of systems $\lambda_b=2,5; 3,3; 3,9$ microns shown in Fig. 1 (curves 1, 2, 3). It is known that contrast filters and slope cutting limits are largely determined by the difference in refractive indices of layers with high n_H and low n_L refractive indices [14]. As a film-forming substance was chosen well-known combination of materials Ge-SiO (respectively $n_H=4,0$ and $n_L=1,85$; $\Delta n=n_H-n_L=2,15$), as well as materials Te-SrF₂ ($n_H=4,5$ and $n_L=1,35$; $\Delta n=3,15$), which is much less used. To filter which can be made of layers of Te-SrF₂, provided the desired large difference of refractive indices of films at the same time in the literature little information on the use of these materials for forming cutting filters, especially in In_4Se_3 crystals and In_4Te_3 .

Such filters are realistic to achieve high optical characteristics – steep short-cut border $K_p=0,93\text{--}0,96$, the maximum bandwidth in the workspace $T_{\max}\geq 90\%$ average transmittance in the region lock background $\tau\leq 10^{-2}\%$. Optimal matching the measured characteristics of the calculated filter with $\lambda_b=3,3$ microns was achieved when used as a substrate crystals In_4Se_3 (Fig. 1, curve 5). Such films had high adhesion and no degradation during thermal cycling to nitrogen temperatures.

This technology temperature determines the structure and density of the film, which is lower compared to the massive crystal and affect properties such as thermal stability, optical thickness, refractive index, strength, mechanical stresses.

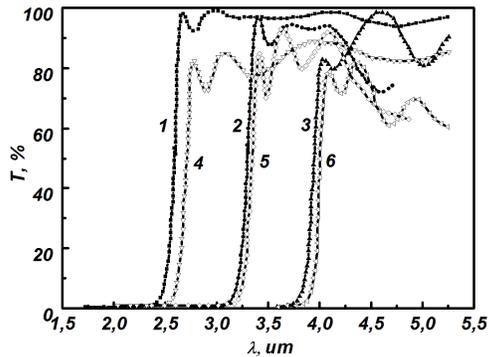
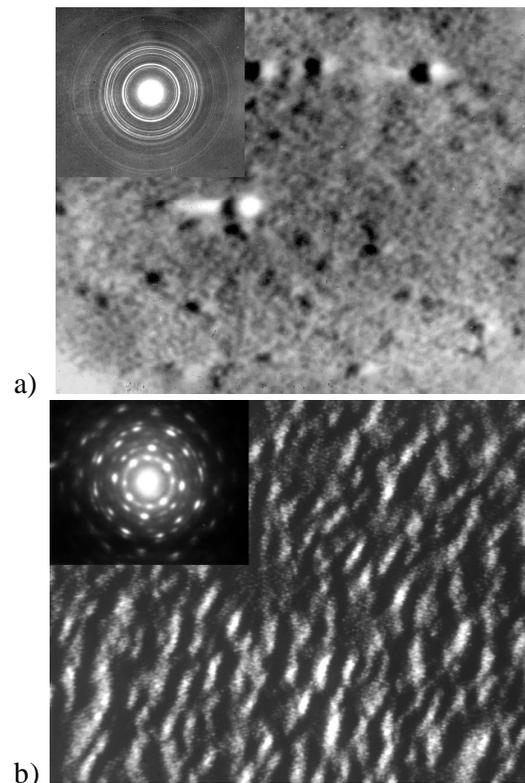


Fig 1. Dependence of the transmission coefficient T filters based $\text{In}_4(\text{Se}_3)_{(1-x)}(\text{Te}_3)_x$ with $\lambda_b=2,5; 3,3; 4,0$ microns of wavelength λ : curves 1, 2, 3 - theoretically calculated curves; 4, 5, 6 - experimental

According to research in the scanning electron microscope SEM-100UA and diffraction EG-100M was found that at substrate temperatures $T_s=403$ K derived amorphous and fine-grained polycrystalline films Te (Fig. 2, a), and at $T_s=523$ K – oriented texture (Fig. 2, b). Such films provide better optical properties interference system. This mode of deposition was used to produce dense, mechanically and temperature stable Te films with low density of drops, that were part of the filter on crystals In_4Te_3 . These values correspond to transmittance requirements industry-removals interference filters.

In Fig. 3 shows the spectral transmission characteristics of the 14-layer filter based on Ge-SiO films, deposited on a plate of In_4Se_3 . On the reverse side the substrate by a three-layer lighting antireflection lining SiO-Ge-SiO was coated. This design interference-absorption filter provides suppression of background radiation in

comparison a narrow range, according to the value of the difference n_H-n_L for these materials. As can be seen from Fig. 3 (curve 1), filters, obtained at low substrate temperatures and in the absence of ion etching, containing defects (Fig. 2, a), had deep dips in spectral characteristic to 50–60% bandwidth. At the same time filter, obtained at the above advanced technology, had spectral characteristics which were average transmittance in the workspace at $> 80\%$ (Fig. 3, curve 2).



**Fig 2. The structure of thin films at different substrate temperatures:
a) $T_s=403$ K; b) $T_s=473$ K;
c) $T_s=493$ K; d) $T_s=523$ K**

For filters with a long wavelength limit cut the substrate In_4Te_3 was applied. This material has a band gap of 0,48 eV, corresponding to the position of the absorption edge of 2,5 microns. Since the range of background suppression in nonworking area of the filter is determined

by absorption in the substrate and in layers, as well as by a range of highly reflective mirrors of interference system, which significantly increases for films with a large value of $\Delta n = n_H - n_L$, were set filters based on the films of Te-SrF₂. It is possible to obtain cutting filters below cut $\lambda_b = 4,0$ microns and $\lambda_b = 6,5$ microns more long-wave region (Fig. 4, curve 1) compared with filters on films Ge-SiO.

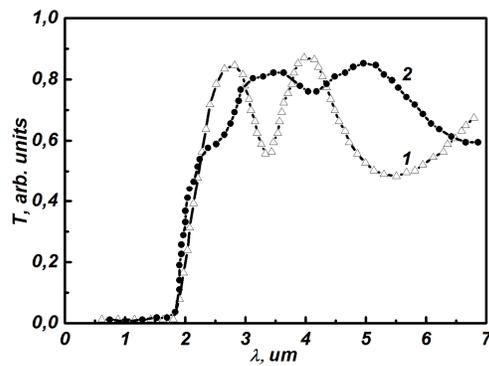


Fig 3. Spectral transmittance characteristics of filters on substrates In₂Se₃: curve 1 at T_s=363K; curve 2 at T_s=423 K

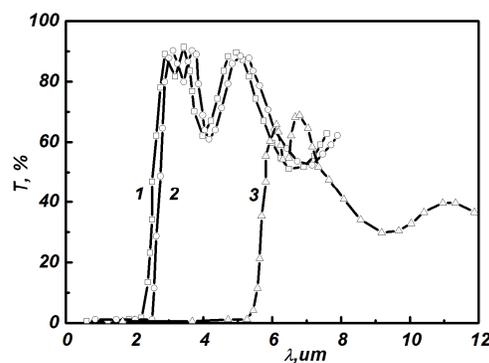


Fig 4. Spectral transmittance characteristics of filters on substrates In₄Te₃: curves 1, 3 at T_s=300 K; curve 2 at T_s=84 K

Investigation of the temperature dependence of the spectral characteristics of the filters showed that cooling to 84 K there is a shift λ_b by 3-4% in the long-wavelength region, as well as some reduction in the average transmission in the workspace (Fig. 4, curve 1 and 2). This

phenomenon can be explained by higher absorption of the films it by cooling and thermal compression of all the films at low temperatures, which causes the difference of optical thickness and index n_H from those values that appear in the theoretical modeling of spectral curves of filters. It should be noted that the magnitude of the displacement of spectral curves does not exceed the values that are put forward appropriate standards for interference-absorption filters.

Have also been developed for two-channel interference filters CdSb had a different design depending on the requirements for conditions of use (Fig. 5). The simplest filter design, which should operate at room temperature, is a combination of absorption filter $\lambda_b = 2,5$ microns (first channel) and on top of it within a given geometric area multilayer interference filter $\lambda_b = 3,9$ um (second channel).

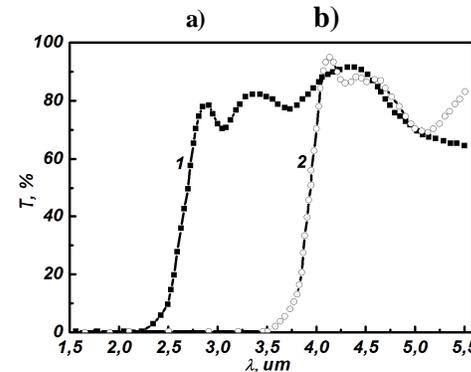


Fig 5. Design (a, b) and experimental transmission characteristics (c) of the interference absorption 24-layer filter on CdSb single crystals: a) single-channel filter, b) two/four-channel coordination-sensitive filter pattern for environmental monitoring (curve 1 – at 293 K, curve 2 – T=83K)

The block diagram of a prototyping of the digital module data processing (Fig. 6) for rapid analysis of changes in transmission or reflection spectra biosensors implemented with dual channel scheme similar to [15, 16]. In this configuration, the first channel is the reference and the other information. When in multiple dimensions, or previous calibration of measuring channel for "zero" indicators

both channels can be informative. The converter of inputting information signal can be implemented as a two-component spectrometric converter. One part is a two-layer structure consisting of reflectivity or missing bases which caused a translucent layer of bio-sensitive material (Fig. 6, area 1 "biosensor" which gets radiation ($h\nu(1)$).

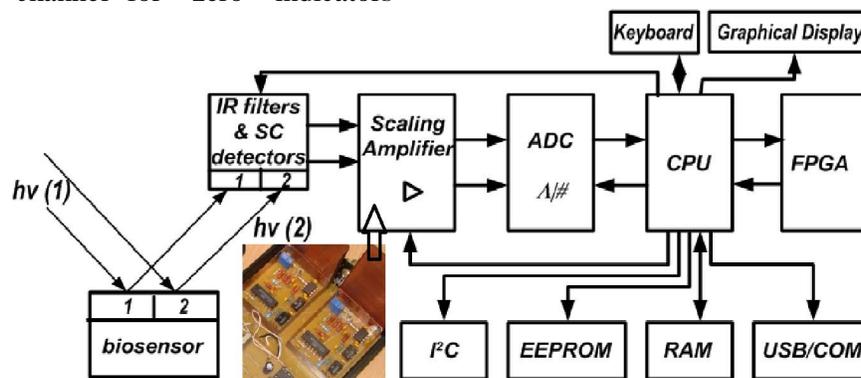


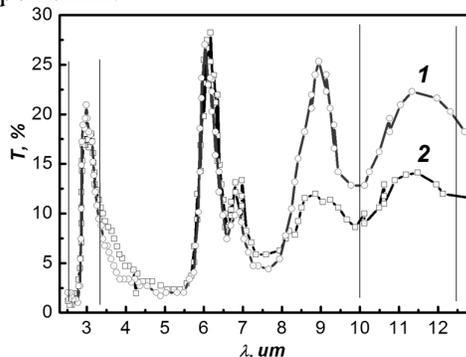
Fig 6. Implementation example reconfigurable microprocessor control module of measurements and digital processing of biosensors signals

Another part – a two-channel semiconductor detector based barrier metal-semiconductor or heterostructure to which cutting through infrared filters of different band (1) and (2) gets reflected from "biosensor" radiation ($h\nu(2)$). In Fig. 6 inset photo shows the layout of dual-channel scaling amplifier. Dynamically change the gain, managing the analog-to-digital conversion, data exchange with peripherals, RAM and special CPU based FPGAs and general management of measurements and data processing is governed by the CPU based on ARM microcontroller. Communication with the computer server is provided through the USB interface. Library files of reconfiguration is downloaded from the server and stored in EEPROM. Reconfiguration of special CPU can be performed manually from the keyboard when you have selected the module or

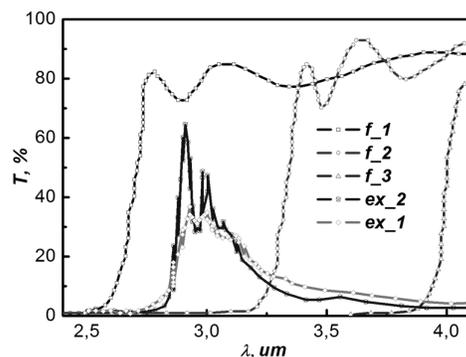
spectrometric transducer, and /or offline according algorithm of the management program. Library files in reconfiguration includes software modules designed for calibration information-measuring device path, numerical calculations of integrated performance ratios reflection / transmission at different wave bands for various test substances and biosensors, and applications of simulation modeling spectra for basic measurements given points in the wave range. The results of rapid processing and analysis can be controlled with a graphical display. The overall indicator value transmission / absorption of radiation in a given wave range is defined as the difference value signals S_0 and $S_{\Delta\lambda}$, measured according to the channels containing the studied range, in which he "cut" IR filter. Thus the measured signal values are adjusted by an amount that takes into account the

deviation spectra radiation source, whose rays irradiated the sample, IR filter transmission spectra and spectra photosensitivity photodetectors from ideal rectangular shape [15].

The experimental spectra of two samples of urea in the range of 2,5 to 12,5 microns (Fig. 7, a) show some deviations in the range of 2,8–5,5 and 8,0–12,5 microns. In [7] the first change in the spectra range from 2.8 to 3.1 microns explain the absorption bands of high protein component of urea, in 10–12,5 micron may manifest elements and compounds penicillin.



a)



b)

Fig 7. Changes in absorption spectra due to urea protein complexes and of penicillin components (a), and (b) - an example of cutting off infrared filters applying for rapid analysis of changes in the spectral characteristics of urea

Integrated performance measurement bandwidth in the area 2,7–4,0 μm for both samples differ within no more than 3–4%, which is within the measurement error and

does not allow state changes in real spectra. Apply filters from outside cutoff of 2,6 and 3,3 μm (Fig. 7, b) allows the shortwave infrared range characteristic of the protein component. The default value is the difference between the measured transmission performance in this case is 12–15%, significantly higher than the total measurement error path device and is sufficient for rapid analysis of the spectra of the samples. As seen in Fig. 7, and is similar to the difference of these indicators for penicillin compounds in the range of 40–50 microns 10–12,5%. For its fixation can be used with the filter cut-off limit of 6,5 microns. This measurement error of the order is consistent with measurement error path, as in the range of 6,5 to 10 microns no "overcompensation" spectra. Of course, to identify specific elements and their teams should conduct a comparative analysis of the fine structure spectroscopy and rapid method it can not replace. To improve the accuracy of rapid analysis should decrease the width of the strip controlled waves and analyze different ranges which manifested the characteristic vibrations of the same group of elements and compounds.

4. Conclusion

At this experiment work was tested two natural sorption materials of inorganic and organic origin in removal of aluminium from water. Sorption capacity of natural zeolite – clinoptilolite was compared with sorption capacity of organic material *Penicilliumglabrum*, one of the worldwide species. Adsorption tests were studied for different initial concentrations of the aluminum in water. Clinoptilolite achieved 93 % efficiency after two hours of contact with water containing aluminium, *Penicilliumglabrum* needed longer time – from seven7 to 9 days to achieve 100% efficiency.

Results obtained from laboratory experiments shown, that both tested materials clinoptilolite and *Penicillium glabrum* effectively removed aluminium from water.

5. References

- [1] WHO: Environmental Health Criteria 194, Aluminium. Geneva, 1997
- [2] BECARIA A., CAMPBELL A., BONDY S.C. Aluminium as a toxicant. *Toxicology and Industrial Health* 18, 309 (2002).
- [3] BARABASZ W., ALBIŃSKA D., JAŠKOWSKA M., LIPIEC J. Ecotoxicology of Aluminium. *J. of Environ. Studies* 11 (3), 199 (2002).
- [4] TOTTEN, G. E.; MACKENZIE, D. S. Handbook of Aluminum. Marcel Dekker. p. 724. (2003).
- [5] CABALLERO B., ALLEN L., PRENKICE A. Aluminium. Encyklopedia of Human Nutrition, 2006.
- [6] WHO: Aluminium in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality, WHO/SDE/ WSH/03.04/53 (2003).
- [7] HELMBOLDT O., HUDSON L.K.: Aluminum Compounds, Inorganic. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, p. 527 (2007).
- [8] BANKS W.A., KASTIN A.J. Aluminum-induced neurotoxicity: alterations in membrane function at the blood-brain barrier. *Neurosci Biobehav Rev.* 13(1), 47-53 (1989).
- [9] FERREIRA P.C, PIAI K.A., TAKAYANAGUI A.M., SEGURAMUÑOZ S.I. Aluminum as a risk factor for Alzheimer's disease. *Rev. Lat. Am. enfermagem* 16, 151 (2008).
- [10] GITELMAN H. J. Physiology of aluminum in man. In: Aluminum and Health, CRC Press, p. 90, (1988).
- [11] YOKEL R.A., HICKS C.L., FLORENCE R.L. Aluminum bioavailability from basic sodium aluminum phosphate, an approved food additive emulsifying agent, incorporated in cheese. *Food and chemical toxicology* 46 (6), 2261 (2008).
- [12] FLATEN T.P., ALFREY A.C., BIRCHALL J.D., SAVORY J., YOKEL R.A.: Status and future concerns of clinical and environmental aluminium toxicology *J. Toxicol. Environ. Health* 48, 527 (1996).
- [13] VULTERIN J., ŠTABLOVÁ R. Toxikológia, bezpečnosť a hygiena práce v chemii. Toxicology, safety and hygiene work in chemistry. Karolinum, Praha (1991).
- [14] HORVÁTHOVÁ E. Properties and Elimination of Ammonium Ions from Water with Natural Zeolites. (In Slovak). *Vodní hospodářství* 7, p. 173-178 (1989).
- [15] BARLOKOVÁ, D., ILAVSKÝ, J.: Natural Zeolites in Water Treatment (In Slovak). *Vodní hospodářství*, 57/6, 213-215 (2007).
- [16] ŠAMAJOVÁ E., KRAUS I.: Prediction of areas of Slovak Zeolites and the possibilities of utilizing them (In Slovak). In: Proceeding of the Conference Slovezo'84, Vysoké Tatry, 1984, pp. 6-10.
- [17] REHÁKOVÁ M., ČUVANOVÁ S., GAVAEVÁ Z., RIMÁR J. Utilization of the Clinoptilolite Type of Natural Zeolite in Agrochemistry and Agriculture (In Slovak). *Chem. Listy* 97, 260-264 (2003).
- [18] BARLOKOVÁ D. Natural zeolites in the Water treatment proces. *Slovak Journal of Civil Engineering* Vol. XVI, Issue 2, 2008, pp. 8-12, Slovak University of Technology in Bratislava 2008, ISSN 1210-3896.
- [19] MERKLE P.B., KNOCKE W.R., GALLAGHER D., et al: Characterizing Filter Media Mineral Coatings, *Journal of AWWA*, 12/1996, s.62-73.
- [20] SAMSON, R.A., HOEKSTRA, E.S., FRISVALD J.C., FILTENBORG O.: Introduction to foodborne fungi. Centralbureau voor Schimmel-cultures Baarn, Ponsen and Looyrn (1996).
- [21] TÓTHOVÁ, L. Occurrence of microscopic fungi in the Slovak section of Danube river. *Biologia*, Bratislava 54/4, 379 (1999).
- [22] FRANKOVÁ, E.: Soil Micromycetes in the Water Environment. *Život. Prostr.*, Vol. 35, No. 3, 156 (2001).
- [23] FRANKOVÁ E., SIMONOVÍČOVÁ A. Geochemically microscopic fungi in polluted environment (In Slovak). *Mineralia Slovaca*, 29, 10 (1997).
- [24] FRANK, V., TÁMOVÁ, G., FARKAS, V., Characterization of white mutant of *Trichoderma viride* obtained by cadmium treatment. *Microbiological Research* 149, 61-64 (1994).
- [25] GADD, G. M. Interaction of fungi with toxic metals. *The New Phytologist* 124, 25-60 (1993).