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Luminescent Behaviour of Monovalent Metals Nitrite/Nitrates incorporated to Microcrystalline Cellulose Matrix by Sorption from Water Solutions

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Abstract

The samples of the microcellulose matrix that contain particles of inorganic oxides, $NaNO_2$, KNO_2, $CsNO_3$ and $AgNO_3$, were made by sorption of these inorganic from the water solutions. Morphology of the concentration sets of such composite materials was studied with use of optical and electronic scanning microscope. The spectra and intensity of photoluminescence of the samples were studied too. It was found that oxides inclusions quench the luminescence of cellulose that can be used in principles for sensing these oxides in water solutions. Manifestation of the characteristics narrow zero-phonon lines in the luminescence of composites samples that contain inclusions of the sodium nitrite, $NaNO_2$, allowed decreasing the limit of this oxide determination down to value $3.5x10^{-3}$ g/l.

Keywords: Microcrystal, Cellulose, Nitrite, Nitrate, Oxide, Luminescence.

1. Introduction

Microcrystalline and microfibrillated cellulose are in use for multifunctional needs and here we would like to draw attention to one of them [1]. It is common knowledge, that cellulose is a very effective sorbent. Despite of the fact that synthetic sorbents based on polyethylene, propylene and other polymers show better performance than cellulose, they are not eco-friendly enough in comparison to cellulose [1-3]. At the same time, cellulose based sorbents can be used not only for removing some materials from liquid or gas. Here we just point an opportunity to use cellulose based materials in bilateral function of both sorbent and sensors for adsorbed compounds determination. Really, some of cellulose materials had been used previously for development of luminescent sensors for inorganic wastes, but the number of similar works is very limited (see [2], e.g.). At the same time, it should be noted that there is a lot of papers devoted to luminescence study of the inorganic oxides incorporated into cellulose materials [4-7]. In should to emphasize that inorganic compounds in noted works had been used for modifications of cellulose fibers properties, for management and control of production or for identification of textile products, paper documents, etc., but not for determination of the inorganic oxides traces in the cellulose or starting materials use for the samples preparation. Besides, in those works luminescence of the cellulose matrix was not used as sensor characteristic. So, first of our work aim is to study opportunity of mentioned application of the microcrystalline cellulose (MCC) use.

Cellulose materials and particularly the MCC among them, are material which reveal at some conditions so-called own photoluminescence (PL). Own luminescence of some material is one that occurs without incorporation of any additive luminescence agents. Manifestations of the own PL of the various cellulose materials are known and described long ago [8-14]. In particular, an influence of some inorganic compounds on the own PL of the MCC was also described and discussed in our previous works [15-17]. Unfortunately, quantitative characteristics, which would determine the effect of very harmful to humans inorganic compounds, for example, nitrites/nitrates ones, in dependence on their concentration in the MCC matrix, however, was not given their. At the same time, if worth no note that determination of of the hazardous inorganic nitrites and nitrates of monovalent alkali metals ($NaNO_2$, KNO_2, KNO_3, $CsNO_3$, etc.) traces in water and soil, e.g., is of high importance [17-19]. In fact, it is known, that high level of nitrites/nitrates, e.g. in the blood, promotes cancerization of hemoglobin. Thus, it is important to have a simple, easy and convenient method for removing these compounds (e.g., by sorption) then followed by a fast eatimation of their amount in water solutions.

Other aim of this work is to discuss an opportunity to create some concentrations scales for the nitrites/nitrates amount determination in water using microcrystalline cellulose as sorbent and luminescence properties of the MCC – oxide composite samples as sensors characteristics

We supposed that use of cellulose based materials for removing of nitrites/nitrates from aqueous solutions and determination of their amount in such solutions by means of luminescent analytical method is promising deal. Moreover, when stating this assumption we had accounted that some of the inorganic nitrites/nitrates also reveal own luminescence and spectral – kinetic characteristics of the luminescence can be very characteristics. Really, as it had been shown in earlier works the series of sharp emission peaks can be observed in the PL spectra of the alkali metal nitrites in their solid water solutions [19-22]. Spectral positions and distances between these peaks are practically insensitive to the type of the host, where nitrites are incorporated. This feature is used for the exact identification of nitrites presence in various materials.

Optical characteristics of the MCC, to a greater extent, and the characteristics of nitrite / nitrates of monovalent metals, to a lesser extent, depend on their pre-history: the ways of production, storage, external environment, etc. So, spectral – luminescent characteristics of used by us initial cellulose and nitrite/nitrates materials were studies in this work one more under concrete conditions of our laboratory. These data we use or comparison as starting characteristics.

2. Samples and Experimental details

The samples, where the microcrystalline cellulose (MCC) is a matrix and nitrite or nitrate oxide such as Sodium Nitrite ($NaNO_2$), Potassium Nitrite (KNO_2), Cesium Nitrate ($CsNO_3$) or Silver Nitrate ($AgNO_3$) was the filler, have been prepared for the luminescent experiments in the next way. First, the tablets of the chemically pure MCC manufactured at ANCYR-B, Ukraine were melt using mechanical milling that was followed by ultrasonic treatment (f = 4.2 kHz) during 20 min. Second, the solutions of different concentrations of the mentioned oxides in distillated water were made. Then, several parts of the same mass of the MCC powder were soaking in the prepared previously oxides solutions for the same time. After, the each wet powder was dried in ambient air conditions and at temperature of 60 C for 16 h following by applying light pressure. As result, durable samples of the composites samples named as MCC-W-Oxide (Oxide = $NaNO_2$, $CsNO_3$, and $AgNO_3$) with disc thickness of near 1 mm and diameter near 10 mm were made. The samples made in the similar way, but if soaking took place in pure distillated water only, were used for comparative study. These samples are named as MCC-W. Started MCC tablettes we have named as MCC-ST. The commercial microcrystalline $NaNO_2$, KNO_2, $CsNO_3$ and $AgNO_3$ powders were used also for

comparative study.

Characterization of the samples morphology was made with use of both optical microscope OLYMPUS GX51 and scanning electron microscope JAMP-9500F Field Emission Auger Microprobe (JEOL, USA) equipped with X-Ray microanalizer INCA PentaFetx3 (Oxford instruments). Microelements analysis of various areas of the samples was also performed using the tools of the same electron microscope.

The PL (photoluminescence) spectra of the samples under study were measured using the spectrometric complex equipment SDL-2M that contains single-grating (1200 grooves/mm) monochromator MDR-23 (linear dispersion 0.5 mm/nm) equipped with FEU-100 photomultipliers. The PL spectra were monitored over a wide range of the emission wavelengths: 300 – 800 nm. The laser radiation of the 337.1, 405 and 473 nm wavelengths was used for the PL excitation. The samples temperatures were 77 or 300 K when their luminescence was registered.

3. Results and Discussion

3.1. Morphology and structure

The samples surfaces were monitored using optical and electron microscopy tools. The Fig. 1 shows some images taken from optical microscope (see upper images *(a)* and (*b*) for the MCC-W (Fig. 1(a) and MCC-W-$NaNO_2$ (Fig. 1(b)) samples as a pattern of such images for another samples under study. Images (*c)* and (*d)* in Fig. 1 shows images of some parts of the respectively mentioned samples obtained by means of SEM. It is easy to see that the MCC-W sample comprise of the conglomerates of near 20 – 50 mcm size. The SEM image clarifies that noted conglomerates consist of smaller agglomerates of near 0.25 – 0.75 mcm size, and the last ones are built by cellulose globules of 5 – 10 nm size. If observe the samples that contain also oxide particles (see images (*b)* and (*d)*) you see similar pictures where shining features indicate obviously incorporated oxide particles. We can state also that oxide particles incorporation change somewhat morphology and size of the MCC elements.

Table 1. The average values of the chemical elements content in the MCC-W and MCC-W-Oxide samples (in at. %)

Sample	C	O	N	Na	K	Cs	Ag
MCC-W	66.01	33.99					
MCC-W, max. value	70.42	36.68					
MCC-W, min value	63.28	29.60					
MCC-W-$NaNO_2$	82.01	16.58	0.42	0.55			
MCC-W-KNO_2	82.08	15.19	0.72		0.96		
MCC-W-$CsNO_3$	76.08	19.74	1.03			1.27	
MCC-W-$AgNO_3$	83.28	13.93	1.24				1.36

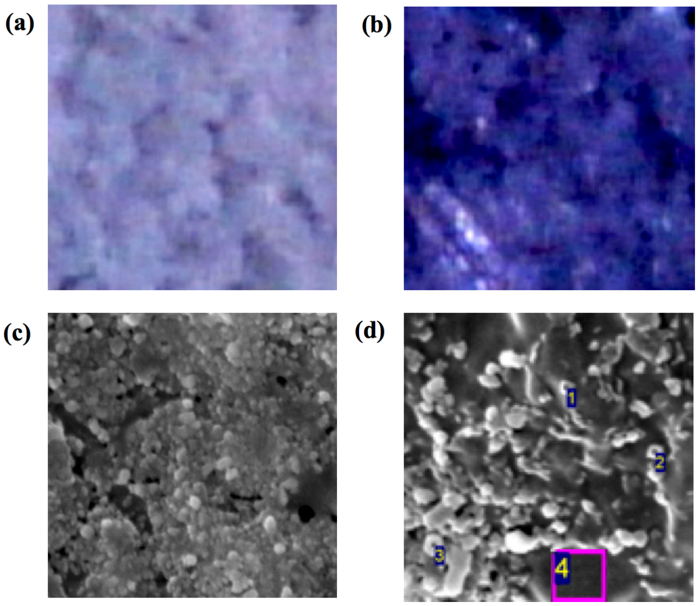

Fig. 1. Optical (a, b) and scanning electronic microscopes images (c, d) of the MCC-W (a, c) and MCC-W-$NaNO_2$ samples (b, d). The size of images is 200 (a, b) and 2 µm (c, d).

3.2. Chemical elements analysis

The analysis of the samples content was made using the tools of the SEM for the several zones of the samples and images of some of those zones are shown on the Fig. 1 where they are marked by rectangles. We can see that the average content of Carbon (C) atoms (the range of its value is 74 – 76 at.% for all of the samples under study) and Oxygen (O) atoms (25 – 23 at.%) is predominant in the zones like to #4 Zone in the Fig. 1(d). Those zones are obvious free of the oxide particles. The zones like to ones indicated as ##1, 2, and 3 on the Fig. 1, where shining details are, contain chemical elements propertied to the corresponding oxides (Table 1). Thus, we confirmed assumption that such type findings just are inclusions of the oxide particles.

3.3. Luminescent properties

The structural and other physical properties of cellulose materials depend on conditions of their preparation (coagulation procedure, drying temperature, type of fixed gas, mechanical and ultrasonic effects), pre-history of the samples, e.g. regeneration from solutions [14, 23, 24]. Mentioned above statement means that MCC luminescence properties depend on the way of the samples preparation, procedures of their functionalization and modification. That is why, starting tablets luminescence as well as luminescence of all other MCC based samples was studied in this work despite of that we have been known about the similar data before published or measured by us recently [15-17].

The measured in this work the PL spectra of the MCC based samples are shown on the Fig. 2. One can see that the PL spectra of starting tablets (MCC-ST) is excited in the wide spectral range from UV (337 nm) to blue light (473 nm) (Fig. 1(a)). (*Room temperature of the samples was applied.*) Undoubtedly, the PL spectra consist of several strongly overlapped components and their superposition, total luminescence band, extends from 350 up to 750 nm.

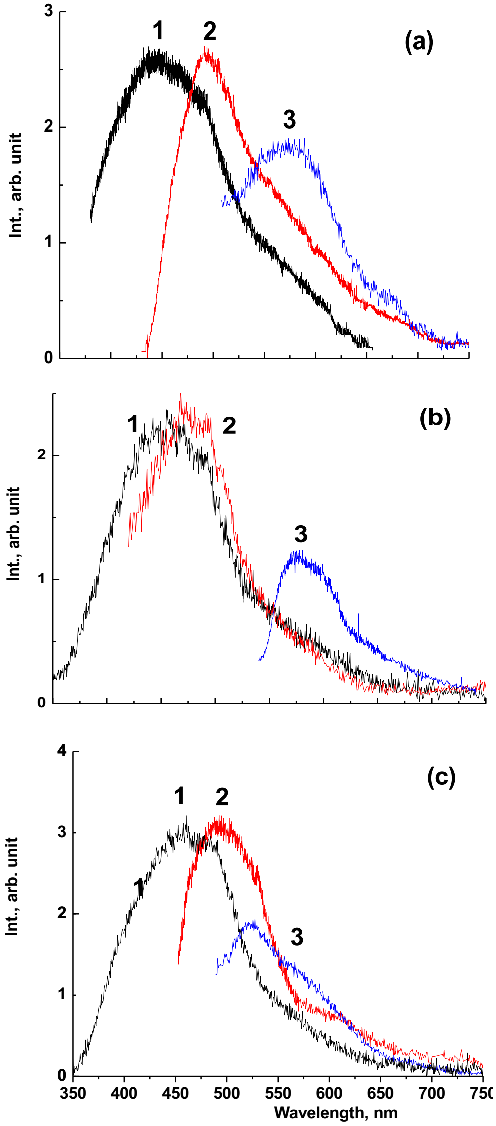

Fig. 2. The PL spectra of the MCC starting tablet's (a), MCC-W samples (b, c) at room (a, b) and 77 K temperatures (c); λ_{ex} = 337.1 (1), 405, and 473 nm (3).

The shape, maximum position, λ_{max}, and total intensity of the PL band and relative intensity of the luminescence components depend on the λ_{ex}: as λ_{ex} increases as the λ_{max} shifts to the long wavelengths side. As result, if λ_{ex} = 337, 405 and 473 nm was used, the spectra with λ_{max} ≈ 425, 500 and 575 nm were measured (Fig. 2(a)). There were found no substantial difference in the luminescence for the MCC-W samples comparing to the MCC-ST samples (see Fig. 2(a) and 2(b)).

As we show below, the need aroused to perform experiments under cooled composite samples, MCC-W-Oxide. So the PL spectra of the MCC-W samples at liquid nitrogen temperature, 77 K, were also measured for the future comparative needs (see Fig. 2(c)). It is easy to see that behavior of the PL spectra at λ_{ex} changing is similar for all described above cases and there were no noticeable changes in the total luminescence intensity.

Described above luminescence properties of the MCC samples are similar to the published data [see, e.g. 8-10, 15-17]. Particularly, the discussed above complex structure of the PL spectra also have showed a manifestation of different nature several luminescence centers in the MCC samples under our consideration. Some types of organic chromospheres in a host matrix of cellulose is usually related to the manifestation of the cellulose based materials luminescence. Those can be carbonyl groups and different kinds of low-molecular derivatives of cellulose destruction.

These results allowed us to predict influence of oxide inclusions on the host luminescence the MCC, when we have planned experiments under composite samples.

Luminescence of the used nitrite/nitrate salts was studied under excitation with various wavelengths. First, the PL of the powder $NaNO_2$ sample was recorded at 300 K and λ_{ex} = 337 nm. The spectrum of mentioned PL lies in the spectral range 400 – 575 nm and at RT shows weekly distinguished fine-structure details like the series of narrow bands located on the wide-band background (Fig. 3, curve 1). (*The peaks of the bands are indicated by arrows on the figure.*) The $NaNO_2$ PL spectra taken under longer wavelength excitation, λ_{ex} = 405 nm, and different attenuation of the luminescence signal receiver are sown as curves 2 and 3 on the Fig. 3. We see the long wavelength side of the spectrum 2 is similar to described above one obtained at λ_{ex} = 337 nm, but an additive luminescence band located in the range 500 – 750 nm was found if we used higher sensitivity of the receiver (Fig. 3, curve 3). Described fine – structure details become clearly distinguished if temperature of the $NaNO_2$ samples decreases down to 77 K (Fig. 3, curve 4).

The nitrates of the monovalent metals are not luminescence active [16, 20–22, 25, 26]. As our own studies had confirmed, the KNO_3 and $CsNO_3$ nitrates did not manifested any luminescence, but they influenced luminescence of the cellulose based materials [15, 16]. Here we also studied $AgNO_3$ and have found its luminescence. The spectrum of the $AgNO_3$ PL is located in the range 475 - 750 nm under excitation with λ_{ex} = 405 nm (Fig. 3, curve 5).

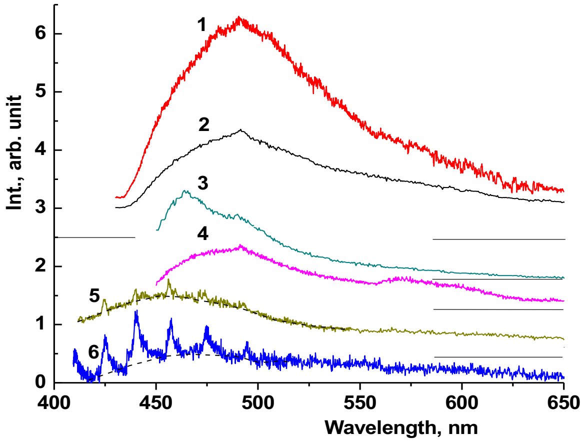

Fig. 4. The PL spectra of the MCC-W-Oxide samples made from the water solutions containing 0.6 (1), 1.1 (2, 6), and $5 \cdot 10^{-3}$ g/l (5) $NaNO_2$; 28.8 g/l $CsNO_3$ (3), and 22.8 g/l $AgNO_3$ (4) at room (1 – 4) and 77 K (5, 6); λ_{exc} = 405 nm.

It is known, an intensive luminescence of one-valence metals nitrites MNO_2 is caused by the radiation transitions from the excited singlet $^1B_1$ level to the ground $^1A_1$ level: $^1B_1 \rightarrow {}^1A$. Spectrum of this PL lies in the range ~ 370 – 550 nm and observed fine - structured details correspond to the phonon-less radiation transitions in NO_2^- molecular anions [16, 20 – 22, 25, 26]. These are so-called zero-phonon lines (ZPL) are accompanied with prolonged phonon wings. The periods of these fine details are determined by the value of the frequency of the molecular anion NO_2^- intra-molecular vibration - ν_2. The ZPL position is described with formula $\nu(n) = \nu_{00} - n\nu_2$, where ν_{00} is the energy of pure electronic transition, and n =1, 2, 3, ... is the number of the ZPL in their series [16]. We have concluded that also that low intensity luminescence found here in the range 500 – 750 nm for the $NaNO_2$ compound is caused by partially allowed radiation transition, $^3B_1 \rightarrow {}^1A_1$, from the excited triplet, $^3B_1$ level, of the NO_2^- anion. This luminescence can be relatively intensive under some special conditions, e.g. as result of the triplet-singlet $^3B_1 \rightarrow {}^1A_1$ transition probability increasing. Thus mentioned data concern of registered by us unusual luminescence of the $AgNO_3$ compound. We think that the manifestation of such PL is related with partial transformation of the MNO_3 compound into MNO_2 under photochemical effect of daylight, scattering laser radiation or radiation of the Xenon lamps used in our experiments. In this case the probability increasing observed for $AgNO_3$ is due to enhancement of the triplet-singlet interaction in NO_2^- anion caused by the Ag^+ cation and NO_2^- molecular anion electronic wave functions overlapping. This is a so-called Z - effect of heavy atom [27]. (*The Ag atom is rather heavier, if compare with the masse of the Na atom.*)

Luminescence spectra of studied MCC incorporated with oxides, named as composite samples, are shown on the Fig. 4. The excitation wavelength equal to 405 nm was taken for these measurements as the most suitable for the study of MCC incorporated with oxides. In fact, we have found rather intensive luminescence of both MCC and oxides and, moreover, the PL spectra of the MCC and oxides are distant at such excitation (see Fig. 2 and 3). When we observed the luminescence of the PL spectra of the composite samples containing nitrite/nitrate salts, then it has been found that the adding of these compounds leads to decrease of the MCC luminescence intensity comparing to luminescence of un-doped MCC-W samples. Analyzing the PL spectra of MCC-W-$NaNO_2$ samples of lower (0.6) and higher $NaNO_2$ concentration (1.1g/l), we state no observable changes of the spectra (Fig. 4, curves 1 and 2). It is easy to conclude that mentioned spectra are similar to measured ones for the case of un-doped MCC. (*You are able to compare curve 2 on the Fig. 2 with mentioned above.*) When composite samples contained nitrates salts, $CsNO_3$ or $AgNO_3$, the PL spectra are change (Fig. 4, curves 3 and 4). As for MCC- $AgNO_3$ luminescence, we see that it's the PL spectrum is a superposition of doped MCC and $AgNO_3$ oxide. So, we can suppose that nitrite/nitrate constituents effect in different ways on the MCC different luminescence sources determining complex character the MCC luminescence. In some cases, like to $AgNO_3$ additive, an own luminescence of oxide can contribute to the luminescence spectra of MCC-W-oxide samples at Room temperature, while the $NaNO_2$ oxide mainly quenches the MCC luminescence.

The PL spectra measured at low temperature, 77 K, for the two component samples, MCC-W-$NaNO_2$, show both MCC and $NaNO_2$ emission simultaneously. Contribution of these two different emissions depends on the $NaNO_2$ concentration in the initial solution (Fig. 4, curves 5 and 6).

Detailed study of the $NaNO_2$ oxide effect on intensity of the MCC-W-$NaNO_2$ samples at T = RT was made and the results of the study are shown on the Fig. 5 (red circles on the curve 1). You can see, if the amount of the $NaNO_2$ in solution is lowering, as changes of the PL

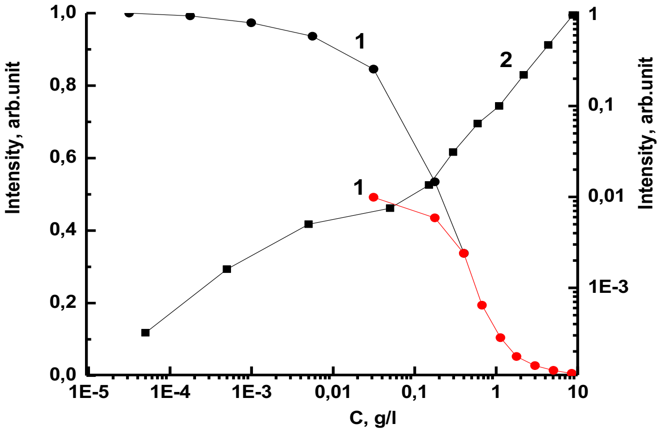

Fig. 5. The dependences of the host (1) and $NaNO_2$ inclusions (2) the PL intensity for the MCC-W-$NaNO_2$ samples on the $NaNO_2$ concentration in water solutions. Temperature of the samples is room – red circles on the curve 1 and 77 K other black symbols; Concentration - in g/l; λ_{exc} = 405 nm.

intensity become weaker. We have noted above that intensity of the MCC luminescence increases if the samples are cooling. Thus, we were able to measure the dependence of the MCC-W-$NaNO_2$ samples luminescence intensity at lower concentration of the $NaNO_2$ using the samples cooled to T = 77 K. (*The contribution of the MCC PL into total luminescence spectra of the* MCC-W-$NaNO_2$ samples *at T = 77 K was evaluated as the area selected under dash line on the curves 5 and 6 on the Fig. 4.*) The dependence is not strong (Fig. 5, curve 1, black circles), if compare with such dependence measured for higher amount of the $NaNO_2$ at Room temperature of the samples. So, we have to conclude that determination of the low amount of the $NaNO_2$ nitrite compound ($\leq 3.5\cdot10^{-1}$ g/l) in the water solution is not reliable.

In order to improve the lowest limit of the sodium nitrite determination in aqueous solutions, we used a change in the intensity of the $NaNO_2$ emission on the $NaNO_2$ concentration in the MCC-W-$NaNO_2$ samples cooled down to 77 K (Fig. 4, curves 5 and 6). Total intensity of the $NaNO_2$ the PL has being determined as part of MCC-W-$NaNO_2$ spectrum like to lying above dash lines near curves 5 and 6 in the Fig. 4; and its dependence on the $NaNO_2$ concentration is shown on the Fig. 5, curve 2. (*Evaluation of the $NaNO_2$ emission intensity for the samples with another $NaNO_2$ amount was made in the same manner.*) We have found that traces of the $NaNO_2$ luminescence can be distinguished in the MCC-W-$NaNO_2$ the PL spectra up to $NaNO_2$ amount in the water solution equal $3.5\cdot10^{-3}$ g/l. We are able to state that it is good result if compare with known ones obtained when complex chemical methods of $NaNO_2$ determination were used [28].

Undoubtedly, our good results are related with manifestation of the series of the characteristics fine details, narrow ZPL lines, in the PL spectra of the $NaNO_2$ compound. These lines are clearly distinguished on the structure-less background of the MCC host luminescence and contrast of the mentioned features is strongly increases if temperatures of the sample are near or lower of 77 K.

4. Conclusions

Two-component samples those comprise from the microcellulose matrix and inclusions of some nitrite or nitrate inorganic oxides ($NaNO_2$, KNO_2, $CsNO_3$ and $AgNO_3$) were made and their morphology, spatial distribution of the inclusions and luminescent properties were studied. The samples were made by preparing aqueous solutions of the above mentioned compounds and following sorption of the compound from solution by dispersed powder of microcrystalline cellulose.

It was found that used oxides influence own luminescence of the matrix in various manner. The measured dependence of the matrix luminescence on the $NaNO_2$ concentration in initial water solution can be used for determination of the $NaNO_2$ amount in water solutions if $NaNO_2$ concentration was not lower than $3.5 \cdot 10^{-1}$ g/l.

The limit of the $NaNO_2$ traces determination in water solution can be lowered if dependence of the $NaNO_2$ luminescence intensity is measured at low temperatures (e.g. 77 K) of the samples. Then, the low limit of the $NaNO_2$ traces in water solution determination become is near $3.5 \cdot 10^{-3}$ g/l.

Future studies have to be performed if we are aimed to enhance sensitivity of the described luminescence method of the nitrite oxides determination in the water. But in any case, the results of this work, in which the cellulosic material was used as an adsorbent, can be considered as the basis for developing more advanced methods for the identification of hazardous substances in foodstuffs of everyday use.

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