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Luminescent determination of nitrite traces in water solutions using cellulose as sorbent

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Abstract. Morphology and photoluminescence (PL) properties for microcrystalline cellulose (MCC), microcrystalline nitrite powders of common formulae MNO_2 ($M = Na, K$) (MCN) and two-component materials composed of both MCC and MCN have been prepared and characterized by means of optical microscopy and luminescence spectroscopy. This study aimed to clarify a possibility of low-limit determination of the nitrite traces in water solutions by luminescent method.

1 Introduction

The fast progress of techniques is accompanied by negative effects on the environment. In this context, detection of hazardous material traces (e.g., drugs, heavy metals, petroleum oils, polycyclic hydrocarbons) in water and soil is of high importance. Nitrites and nitrates are also known as toxic pollutants of environment, plant-based food and biological systems (Fanning, 2000; Zhou and Wang, 2012). In fact, the high level of nitrites in the blood promotes the cancerization of hemoglobin. So, it is undoubtedly important to use a simple, easy and convenient method for removing these compounds (e.g., by sorption), followed by a quick estimation of their concentration in solutions.

According to recommendations of the World Health Organization, the amount of nitrites in water should not exceed $3\,\mathrm{mg\,L^{-1}}$, while for nitrates the corresponding value is $50\,\mathrm{mg\,L^{-1}}$ (*Guidelines for drinking-water quality* – 4th ed. Geneva, Switzerland, 2011). Available methods satisfy the parameters of determination of nitrite content in solutions. The limits for detection are 0.005–$0.01\,\mathrm{mg\,L^{-1}}$ for the molecular absorption spectrometric method, $0.035\,\mathrm{mg\,L^{-1}}$ for ion chromatography and $0.05\,\mathrm{mg\,L^{-1}}$ for liquid chromatography. However, the methods listed above require pretreatment involving application of additional chemical reagents. LED (light emitting diode)-sourced optical fiber sensor, based on evanescent wave absorption, allows measuring a nitrite concentration higher than $10^{-3}\,\mathrm{mg\,L^{-1}}$ (Suresh Kumar et al., 2002). The main disadvantage of absorption-based methods of nitrite traces determination is associated with the absence of characteristic peculiarities on the absorbance spectra of water solutions. The presence of some other contaminant in a solution can lead to absorption changes and affect the accuracy of nitrite concentration estimation.

It has been shown in earlier works (e.g., Kononenko and Kushnirenko, 1980) that the series of sharp emission peaks in luminescence spectra of alkali metal nitrites can be observed. Spectral positions and distances between these peaks are practically insensitive to the type of the host where nitrites are incorporated. This feature can be used for the exact identification of nitrates present in various materials. This work extends the approach on nitrite immobilization from water solutions in cellulose to reveal their presence through the luminescent method.

It is common knowledge that cellulose is a very effective sorbent. Really, synthetic sorbents based on polyethylene, propylene and other polymers show better performance, but they are not eco-friendly enough in comparison to cellulose. Cellulose is a material widely used and it is also considered as an inexhaustible source for manufacturing biocompatible products. The range of cellulose's promise spreads from "paper electronics" ("paper transistor" on a carbon nanotube or organic LED), based on luminescent cellulose (Yun et al., 2009; Karakawa et al., 2007; Pikulev et al., 2012) to forensic examination and eco-friendly sorbents suitable for sorption and stabilization of a wide range of various types of materials (Konstantinou et al., 2006; Chukova et al., 2005). This variety of possible applications is determined by the porous, micro- and nanostructured morphology of the cellulose host and by the unique nature of its interaction with other chemical compounds (Glikman and Somova, 1964; Zugenmaier, 2008; Kovalenko, 2010). The physical properties (in particular, optical properties) of cellulose are dependent on its degree of crystallinity. It is worth noting that cellulose is, like many other polymers, partially crystallized. Its crystallites are long-ordered but its molecular chains do not have an ideal tridimensional structure; in other words, the crystallites are defective. The degree of crystallinity and the chain's order depend on conditions of cellulose preparation (coagulation procedure, drying temperature if $T > 200\,^{\circ}\mathrm{C}$, type of fixed gas, mechanical and ultrasonic effects) and is lower after cellulose regeneration from solutions (Glikman and Somova, 1964; Zugenmaier, 2008; Kovalenko, 2010; Yun et al., 2009; Karakawa et al., 2007; Pikulev et al., 2012). Taking into account that the proposed method of nitrite traces determination deals with a composed material, cellulose + nitrite, it is clear that luminescence properties of pure cellulose should be studied in the first stage of investigation.

2 Samples and experimental details

There were four types of cellulose samples used for the study. Sample #1, labeled CT, was the starting tablet of chemically pure microcrystalline cellulose (MCC) manufactured at ANCYR-B, Ukraine. The next samples, CD, were prepared from the CT samples by their dispersion using mechanical milling of the cellulose tablet followed by ultrasonic treatment ($f = 4.2\,\mathrm{kHz}$). Then, the powder was pressed into a disk using light pressure. Samples #3, or CDW, were made from the CD samples in a two-stage treatment. The first stage of the preparation was soaking of the CD sample in distilled water, followed by applying sufficient light pressure to obtain a durable sample with disc thickness of close to 1 mm. Afterwards, the CDW samples were dried in ambient air conditions at a temperature of 60 °C for 16 h. The soaking of the CD sample in a water solution of nitrites, MNO_2 (M = Na, K), was followed by the described-above pressing and drying procedures used to make the disk of composite material, cellulose + nitrite, producing sample #4, named Cell-NO. The luminescence of the microcrystalline $NaNO_2$ powders (MCN) was investigated for comparison, too.

A set of the microphotos of the above samples was made with the optical microscope. The PL (photoluminescence) spectra and PL excitation were measured using the spectrometric equipment SDL-2M. The PL spectra were studied as a function of the exciting radiation wavelength (λ_{ex}) and were analyzed over a wide range of excitation and emission wavelengths (200–800 nm) and sample temperatures (77–300 K). The PL emission spectra were analyzed using a single-grating (1200 grooves mm^{-1}) monochromator MDR-23 (linear dispersion 0.5 mm nm^{-1}) equipped with a FEU-100 photomultiplier. The N_2 laser ($\lambda_{ex} = 337.1\,\mathrm{nm}$), two diode-pumped lasers ($\lambda_{ex} = 473$ and 532 nm, respectively) and a xenon lamp (DKsSh-150) were used as sources of PL excitation. The results were compared with known literature data and with results of our own investigation of the same luminescent analytes incorporated to some other solid matrixes (see Kushnirenko et al., 1984; Belii et al., 1984; Kononenko et al., 1985). During the measurements at $T = 77\,\mathrm{K}$, the samples were put into liquid nitrogen cryostat. A fast plunge from nitrogen vapors at a higher part of the cryostat to liquid nitrogen at the bottom of it allowed avoiding icing at the surface of the samples.

3 Experimental results and discussion

3.1 Morphology of the samples under study

Figure 1a shows an image of a cellulose tablet surface (sample #1, CT). It is clearly seen that the tablet is a conglomerate of amorphous-phase and evenly distributed microcrystals with a predominant size of ∼ 20–40 µm. Dissolution in water after dispersion (sample #3, CDW) leads to cellulose fluff-out and following disassimilation into an ensemble of flakes with sizes from 10 to 100 μ (Fig. 1b). The flakes consist of a great number of 2–3 μ microglobules.

The MCN samples represent a set of microcrystals randomly distributed over the surface of glass substrate (Fig. 1c). The predominant size of the crystal grains is approximately 20–40 μ.

Finally, a two-component composite Cell-NO (sample #4) is strongly heterogenic. The areas similar to the mixture of the $NaNO_2$ particles and cellulose (Fig. 1d) and the areas that consist of large transparent jelly-like cellulose grains (their size is near 200 μ), with a great number of smaller 5–20 μ inclusions (Fig. 1e), are also found. We can expect that the last ones are the inclusion of the $NaNO_2$ particles into the cellulose host. It is easy to see that the morphology and sizes of MCN grains in the "free" powder and in the composite are different. In the first case, the crystals have similar sizes in all three directions, while in the second case the crystals have various shapes and sizes. These changes are obviously the result of the cellulose lattice effect on MCN crystals. This fact shows that the cellulose + $NaNO_2$ composite is not only a mechanical mixture of two components – cellulose and $NaNO_2$ crystallites.

3.2 Luminescence properties

Physical properties as well as the degree of crystallinity and chain order of cellulose-based materials depend highly on conditions of the manufacturing and treatment procedure.

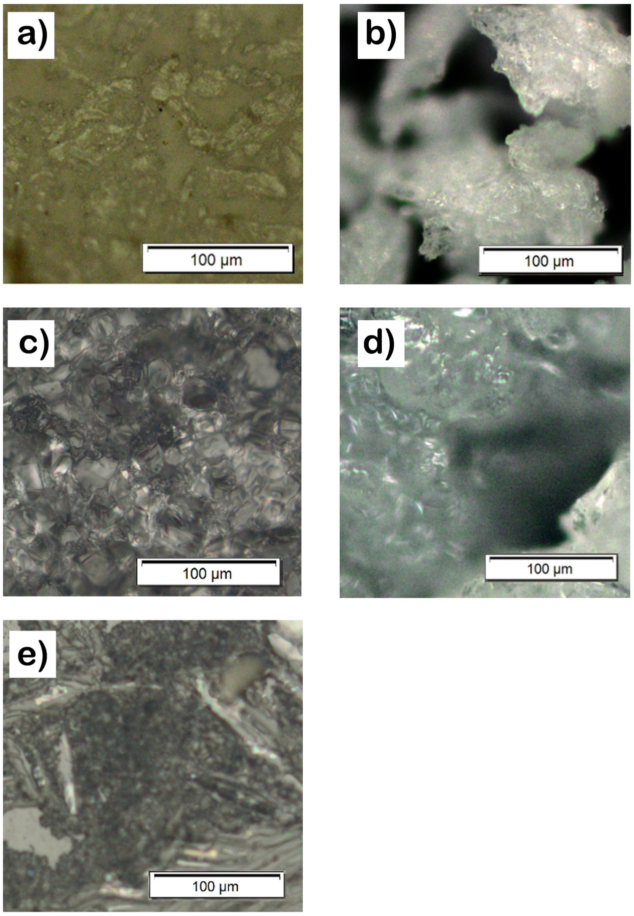

Figure 1. Optical microscopy images of the cellulose tablet, CT sample **(a)**; dispersed cellulose, CDW sample **(b)**; $NaNO_2$ powder **(c)**; and a composite Cell + $NaNO_2$ sample taken in two different areas **(d, e)**.

Thus, we have performed experiments on luminescence spectroscopy for our cellulose samples.

All the cellulose samples are characterized with intensive PL. The widely composed emission band located in the 325–750 nm range is observed in the PL spectra of cellulose samples #1–3 under excitation in a wide range of excitation wavelengths, λ_{ex}: 300–532 nm (Figs. 2, 3). The shape, peak position and intensity of the PL band depend on the λ_{ex}. The dependences of the spectra on λ_{ex} have a similar character for the mentioned cellulose samples: as λ_{ex} increases as the peak position, λ_{max}, reveals a tendency to the long wavelength side shifting of the spectra (see Figs. 2, 3). Mainly, the component with the peak position, $\lambda_{max,}$ near 430–470 nm dominates in the spectra at UV excitation. It is clearly seen for the dispersed cellulose sample CD (Fig. 2b). An additional band is also observed if visible radiation (λ_{ex} = 450–530 nm) is used for PL excitation. The band is situated at longer wavelengths than UV excitation is. This is a range of 500–700 nm and the λ_{max} of the band is near 680–590 nm (Figs. 2, 3b, spectra 5).

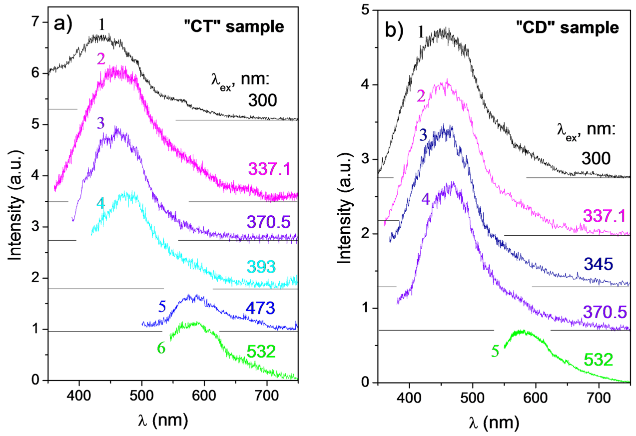

Figure 2. The PL spectra of the samples CT **(a)** and CD **(b)**; λ_{ex} = 300 (**a**, 1; **b**, 1), 337.1 (**a**, 2; **b**, 2), 345 (**b**, 3), 370.5 (**a**, 3; **b**, 4), 393 (**a**, 4), 473 (**a**, 5) and 532 nm (**a**, 6; **b**, 5); T = 300 K.

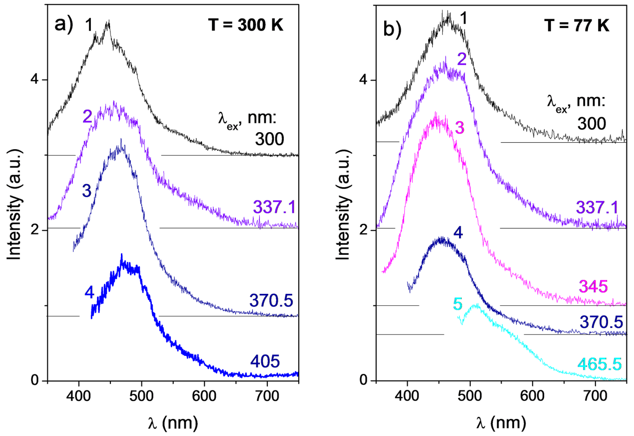

Figure 3. The PL spectra of the CDW samples at 300 **(a)** and 77 K **(b)**; λ_{ex} = 300 (**a**, 1; **b**, 1), 337.1 (**a**, 2; **b**, 2), 345 (**b**, 3), 370.5 (**a**, 3; **b**, 4), 405 (**a**, 4), and 465.5 nm (**b**, 5).

As luminescence of alkali metal nitrite and impure NO_2^- molecular anions are more distinctive at low temperatures (T < 300 K), the PL properties of cellulose samples taken after dissolution in water, CDW samples, were monitored at both room and liquid nitrogen temperature (77 K). When temperature of the samples decreases from 300 to 77 K, the change of PL spectra is small (compare Fig. 3a and b). At observed low temperatures the PL is mainly excited in the UV–V region of light: 300–405 nm.

The PL spectra of the powder microcrystalline salts, NO_2 (M = Na, K), were recorded at 300 and 77 K (Fig. 4). These spectra at RT (room temperature) show fine-structure details like the series of narrow bands placed on the wide-band background. The bands are clearly distinguished for the $NaNO_2$ case (Fig. 4, curve 1). That is why posterior studies were performed using sodium nitrite, $NaNO_2$, compounds. The contrast of the mentioned bands strongly increases if temperature

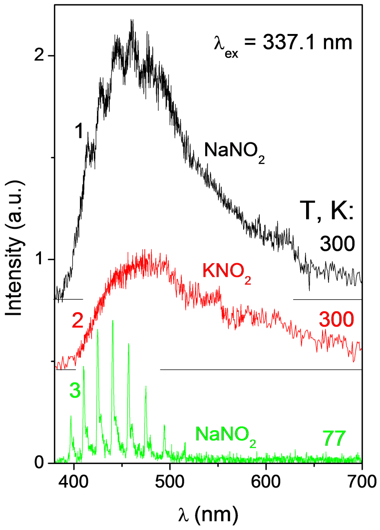

Figure 4. The PL spectra of the $NaNO_2$ (1 and 3) and KNO_2 (2) samples; $T = 300$ (1, 2) and 77 K (3); $\lambda_{ex} = 337.1$ nm.

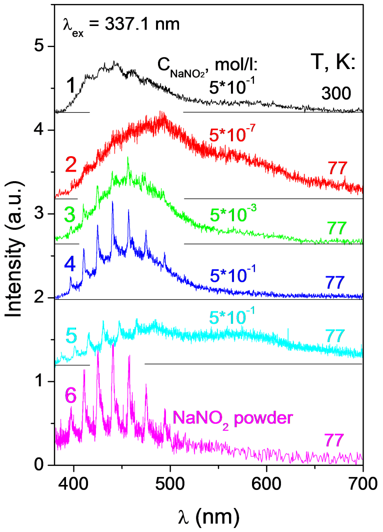

Figure 5. The PL spectra of the cellulose–$NaNO_2$ composite samples #4, Cell-NO, (1–5) and $NaNO_2$ powder (6); $\lambda_{ex} = 337.1$ nm; $T = 300$ (1) and 77 K (2–6). The concentrations of the $NaNO_2$ salts in water solutions were 5×10^{-1} (1, 4, 5), 5×10^{-3} (3), and 5×10^{-7} mol L^{-1} (2). The spectra 4 and 5 were taken for the sample areas shown in Fig. 1d and 1e, respectively.

of the sample decreases. Then, the spectrum shows the series of narrow lines, each of them accompanied with a longer wavelength shadow (Fig. 4, curve 3).

The PL spectra of the composite samples containing $NaNO_2$, Cell-NO, show a weak fine structure at $T = 300$ K. When temperature decreases down to 77 K, distinctive series of the lines appear (Fig. 5, spectra 3–5). It should be noted that concentrations of the $NaNO_2$ salts in the initial water solutions were high: 5×10^{-1} mol L^{-1} (Fig. 1, spectra 3–5). So, the $NaNO_2$ concentration was the same for three spectra – 3, 4 and 5 – taken at the same condition. At the same time, the $NaNO_2$ concentration in initial water solutions was only 5×10^{-7} mol L^{-1} for the case of the spectrum 2 in Fig. 5.

The previously escribed luminescence peculiarities of cellulose samples #1–3 are similar to those reported earlier in the literature (Gavrilov and Ermolenko, 1966). For example, our findings prove that there are several luminescence centers in the studied cellulose samples. This circumstance determines the fact that PL spectra contain several components with peak positions near 360, 430, 465 and 580 nm and their contributions to the total spectrum depend on the λ_{ex} (Figs. 2, 3). The mentioned multicomponent structure of the PL bands is usually related to the presence of several types of organic chromospheres in a host matrix of cellulose. There can be carbonyl groups and different kinds of low-molecular derivatives of cellulose destruction. Taking this into account, we are not surprised that the incorporation of nitrite compounds into the cellulose host matrix will change the PL properties (compare Figs. 3 and 5).

The fine-structure details obtained for MNO_2 and Cell-NO samples correspond to the phononless radiation $^1B_1 \rightarrow {}^1A_1$ transitions in NO_2^- molecular anions. The periods of these details, so-called zero-phonon lines (ZPL) accompanied with phonon wings, in the series are determined by the value of NO_2^- intra-molecular frequency – ν_2. It is worth noting that there is one similar series of lines in the cases of the 1–4 spectra in Fig. 5, and that the positions of the lines are close to the ones for the $NaNO_2$ powder sample (Fig. 5, curve 6). Moreover, in the case of the spectrum 5 in Fig. 5 additional series dominate in the spectrum. The ZPL positions for each series, $\nu_n^{1,2}$, are described with formula $\nu_n^{1,2} = \nu_{00}^{1,2} - n\nu_2^{1,2}$, where ν_{00} is the energy of pure electronic transition, and $n = 1, 2, 3, \ldots$. It was found that $\nu_2^1 = 826\,\mathrm{cm}^{-1}$ and $\nu_{00}^1 = 26\,840\,\mathrm{cm}^{-1}$ for the first series of ZPL and $\nu_2^2 = 868\,\mathrm{cm}^{-1}$ and $\nu_{00}^2 = 27\,570\,\mathrm{cm}^{-1}$ for the second one. It is worth noting the last parameters are very close to the ones for the series of ZPL in the PL spectrum of the $NaNO_2$ powder sample: $\nu_2 = 824\,\mathrm{cm}^{-1}$ and $\nu_{00} = 26\,838\,\mathrm{cm}^{-1}$.

Thus, we can conclude that the PL spectra of the two-component samples show both cellulose and NO_2^- emission simultaneously. Contribution of these two different emissions depends on the $NaNO_2$ concentration in the initial water solution and of the sample #4 area taken for monitoring (Fig. 5). It is known that luminescence spectra of the MA (molecular anion) NO_2^- in solid water solutions reveal several components caused by NO_2^- ions located in various structurally different phases of solid solutions. There are several types of PL centers where MA NO_2^- are the core, but are located in different neighboring spaces (Kononenko et al., 1985; Belii et al., 1985, 1988). It is obvious that the formation of the several types luminescence centers based on NO_2^- anions is possible in the case of the cellulose compositesample #4. First, there can be the centers formed by MA NO_2^- located in the volume of the MNO_2 particles. These centers have to reveal spectral features similar to the cases of metal alkali nitrite salts and alkali–halide crystals doped with MA NO_2^- (Sidman, 1957; Brooker and Irish, 1971; Kushnirenko et al., 1984; Belii et al., 1984, 1988; Kononenko et al., 1985). Such type centers dominate PL emission of the area shown in Fig. 1d. Second, there can be the centers formed by NO_2^-, which are located near surface of mentioned particles. These NO_2 groups can be related to nearby atoms that belong to the cellulose matrix. Finally, the third type of luminescence centers is formed by the "isolated" NO_2^- molecular anions that are adsorbed by the cellulose host. The first and second types of centers can be responsible for the two observed series of ZPL in the PL spectra. The third type of centers can create a structureless band that manifests in the range 520–620 nm in the PL spectra of the Cell-NO sample #4 (Fig. 5). The facts mentioned above indicate interaction between the host matrix and nitrite component of the composite material.

From the analytical point of view, it is easy to conclude that spectra like #4 in Fig. 5 are the most suitable for low-limit determination of sodium nitrite in water solutions.

Furthermore, we would like to emphasize the "energetic" interaction between the mentioned components of the composite sample: the cellulose host matrix luminescence covers the spectral region where excitation of the NO_2 groups takes place (Kononenko et al., 1985; Belii et al., 1985, 1988). So, there is an opportunity for excitation energy transfer from cellulose host to luminescent NO_2^- molecular anions. This fact promotes the enhancement of the NO_2^- molecular anion luminescence intensity. Therefore, we were able to detect NO_2^- emission for the samples Cell-NO obtained from a $NaNO_2$ water solution where the concentration was $5 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ or $0.035\,\mathrm{mg\,L^{-1}}$ for $NaNO_2$ nitrite compounds (Fig. 5, curve 2). Obtained results show the proposed luminescence-based method for nitrite trace determination has sensitivity similar to methods reported in the Introduction. The proposed method is simple and can be applied in some cases when the possibility of using other techniques is restricted for some reason (e.g., absence of required chemical reagents). We suppose that specially before prepared "cellulose serviette" can be used as a selective device, which reacts by means of luminescence signal, change on the nitrite compounds incorporation. The obtained lower limit for a nitrite trace to be identified is high enough (in comparison with the usual methods); so, we think cellulose can be used not only as sorbent but also as sensing material for nitrites. Therefore, such a device can be regarded as a chemical sensor and can be of interest for the sensor systems community. It is worth noting that luminescence spectra should be obtained for various areas of a cellulose + nitrite sample in order to avoid influence of partial crystallinity effects.

At present we have no certain data of other substances such as heavy or transition metal ions showing wide luminescence spectra and influence over their own cellulose luminescence. As for RE (rare earth) ions, they manifest well-known linear spectra at the UV region of the PL excitation and we did not find any trace of the RE ions' luminescence. The possibility that the luminescence determination of other hazardous materials which can be absorbed by cellulose will be a subject of further investigations.

4 Summary

The method of determining the nitrite compound traces via their sorption by cellulose using luminescent properties of the NO_2^- molecular ion has been developed, and the low limit of the $NaNO_2$ determination in water solution was evaluated as $5 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ ($0.035\,\mathrm{mg\,L^{-1}}$). Further studies of cellulose + MNO_2 (M = Na, K, Cs) composite materials have to be performed to determine the most suitable conditions of analytical performance.

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