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Luminescent chemosensor for detecting dimethylamine and ammonia vapors

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The interaction of tris-dibenzoylmethanate Eu(III) with dimethylamine and ammonia vapors was investigated. It was found that when vapors of aqueous solutions of analytes are exposed to tris-dibenzoylmethanate Eu(III) impregnated into the SiO_2 matrix, an optical response is observed in the form of an increase in the luminescence intensity of Eu(III). Changes in the luminescence spectra and luminescence excitation of this sensor are analyzed, both under the quenching action of water vapor and under the sensitizing action of analyte vapors. The main points recorded in the excitation spectra are noted, which are important for understanding the processes occurring in the near environment of the lanthanide center. The luminescent chemosensor is promising for creating sensors for detecting ammonia and amines in food safety control and environmental monitoring.

Keywords: europium(III), beta-diketonates, luminescence, ammonia, dimethylamine, sensors.

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Introduction

Currently, intensive research is being carried out in the field of developing polyfunctional materials with optical chemosensory properties [1–4]. Analysis of literature data demonstrates that promising compounds to produce optical chemosensors are metal compounds [5,6], in particular, lanthanide-containing compounds with luminescent properties [7–14].

The advantages of the luminescent sensor method include the low dependence of the signal on electrical, magnetic and radiation interference, the ability to reliably seal the luminescent detector-analyzer, which makes it possible to record the luminescent response in aggressive environments or at considerable distances. [7,15]

Water molecules are effective luminescence killers, so removal or replacement of coordinated water molecules, as a rule, leads to a change in the luminescence intensity and the lifetime of the excited state of the lanthanide ion [16,17]. Displacing the bonded water molecule from the lanthanide center is a fruitful strategy for developing lanthanide-based chemosensors.

Development of chemosensor systems for such analytes as ammonia and volatile amines is of particular interest for practical applications. Ammonia is used in huge quantities in the chemical industry (for production of fertilizers, explosives, polymers, nitric acid, soda). Liquid ammonia is used in refrigerators as refrigerant, as well as in chemical production as solvent. Ammonia is toxic, even small amounts of the substance have a detrimental effect on living organisms [15]. In connection with intensive growth of housing construction, an acute environmental problem has emerged associated with emission of ammonia and amines from building and finishing materials and concrete structures as one of the sources of both short-term and long-term chemical pollution of air in residential premises. As a result of air pollution, the quality of the housing indoor environment is steadily declining and the number of people with allergic and other diseases [18–20] is growing.

Synthetic amines are produced in the amount of millions of tons annually and are widely used in agriculture, pharmaceuticals and food industries [15,21]. Biogenic and volatile amines are also often formed as a result of decomposition of amino acids in metabolic processes, and their abnormally high concentrations can indicate food spoilage [22,23]

As a continuation of our articles on the study of the chemosensory properties of Eu(III) complex compounds [24–26], this article presents the results of a study of the water vapor, ammonia and dimethylamine effect on the luminescence of the chemosensor $Eu(Dbm)_3 \cdot H_2O$, where Dbm — dibenzoylmethanate anion.

Experimental part

Eu(III) tris-dibenzoylmethanate was synthesized according to the procedure described in [27]. The complex compound was obtained by reaction of $Eu(NO_3)_3 \cdot 6H_2O$ and dibenzoylmethane with molar ratio of 1:3, mixing of solutions of pure substances in absolute ethanol when heating. Subsequently, the final solution was neutralized (up to pH8) by dropwise addition of ethanolic ammonia

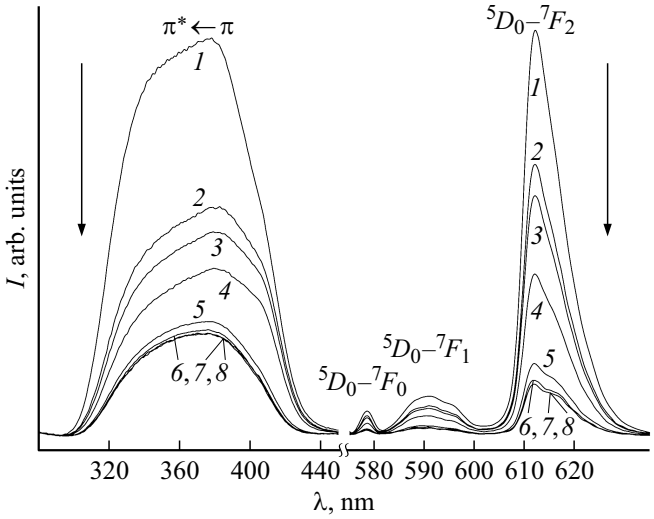

Figure 1. Luminescence excitation and luminescence spectra of a chemosensor exposed to water vapors. Luminescence spectra: *1* — 0, *2* — 26, *3* — 38, *4* — 86, *5* — 326, *6* — 602, *7* — 900, *8* — 1800 s. Luminescence excitation spectra: *1* — 0, *2* — 30, *3* — 56, *4* — 108, *5* — 342, *6* — 576, *7* — 888, *8* — 1770 s.

solution. The resulting yellow precipitate was filtered off, washed with ethanol, and dried in air.

PTSKh-AF-A thin-layer chromatography plates (manufactured by Sorbfil) were used as a matrix for impregnation of the Eu(III) complex. Samples were obtained by depositing solution of Eu(III) tris-dibenzoylmethanate in acetone ($C = 1 \cdot 10^{-4}$ M) onto this matrix and keeping it in dry atmosphere for 30 min until the solvent completely evaporated. The samples were carefully packed in polyethylene in a desiccator over SiO_2.

Sample luminescence and luminescence excitation spectra were recorded using RF-5301 spectrofluorometer (Shimadzu). To detect the luminescent response, the samples were placed in an optical cell with a lid (cell thickness 1 cm, height 4 cm), to which 1 drop (0.05 ml) of aqueous solution of ammonia or dimethylamine was added to create certain saturated vapor pressure; the cell was thermostated at 20°C, pressure coupling was absent.

Results and discussion

The strong quenching action of water vapors on luminescence is evidenced by the data in Fig. 1, based on which it can be seen that under the action of water vapors, almost complete quenching of luminescence is observed (the luminescence intensity of the model sample of the chemosensor decreases within 10 min by 8 times).

It should be noted that after drying the chemosensor sample, the luminescence intensity is completely restored, which was confirmed in the articles [24,25].

In contrast to water vapors, when vapors of aqueous solutions of ammonia and dimethylamine acts on the chemosensor, an increase in the luminescence intensity is recorded, i.e. despite the presence of water vapors, ammonia and dimethylamine themselves produce a sensitizing effect (3D collage in Fig. 2, where *a* — dimethylamine and *b* — ammonia). Based the data in Fig. 2, which shows the evolution of the luminescence excitation spectra as a function of time, a complex sequence of spectrum envelope transformations is recorded.

Let us consider in more detail the effect of vapors of aqueous solution of dimethylamine on a chemosensor sample. It can be seen from the data in Fig. 2, *a* and Fig. 3 that in the initial period of exposure to analyte, a rapid increase in the luminescence intensity is observed without rearrangement of the Stark components of the spectrum.

This indicates that the sensitizing effect of the analyte on the $Eu(Dbm)_3 \cdot H_2O$ model chemosensor in the initial period occurs without explicit rearrangement of the inner sphere of Eu(III) and manifests itself in enhancement of the antenna effect due to an increase in the efficiency of ligand-metal energy transfer [7]. Such a reversible action is characteristic of many volatile amines and ammonia even at minimal analyte concentrations (~ 5 ppbv), as shown earlier [24,25].

With further exposure to dimethylamine vapors, a short-term decrease in the luminescence intensity is observed with a change in the Stark structure of the luminescence spectra and a noticeable change in the structure of the luminescence excitation spectra (Fig. 2, *a*). This may indicate a clear rearrangement of the inner coordination sphere Eu(III). Decrease in the luminescence intensity during this period is mainly caused by the quenching action of water molecules.

Later on, with time, the luminescence intensity increases with reaching a plateau. This indicates that the quenching action of water vapor reaches a plateau and the processes of luminescence sensitization under the action of dimethylamine vapors prevail. Rearrangement of the inner coordination sphere of Eu(III) and the change in the symmetry of the crystal field of the nearest surrounding of europium are indicated by the change in the Stark structure of the $^5D_0$–$^7F_0$, $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions (Fig. 3, insertions). In addition to the change in the Stark structure, the $^5D_0$–$^7F_2$ transition under the action of the analyte is characterized by a distinct bathochromic shift of the luminescence band (~ 1 nm).

Let us consider the effect of aqueous ammonia solution vapors on a chemosensor model sample. Based the data in Fig. 2, *b*, which shows the evolution of the luminescence excitation 3*D*-spectra as a function of time, it can be seen that under the action of ammonia, a complex sequence of spectrum envelope transformations is recorded.

Figure 4 shows the evolution of the luminescence excitation and luminescence spectra of the chemosensor under the action of ammonia. Over time, a gradual increase in the intensity of the spectral bands is observed: after 15 min of exposure to the analyte, the luminescence intensity of the electric dipole transition $^5D_0$–$^7F_2$ increases by 10 times. In this case, radical changes in the structure of the luminescence excitation band are observed: over

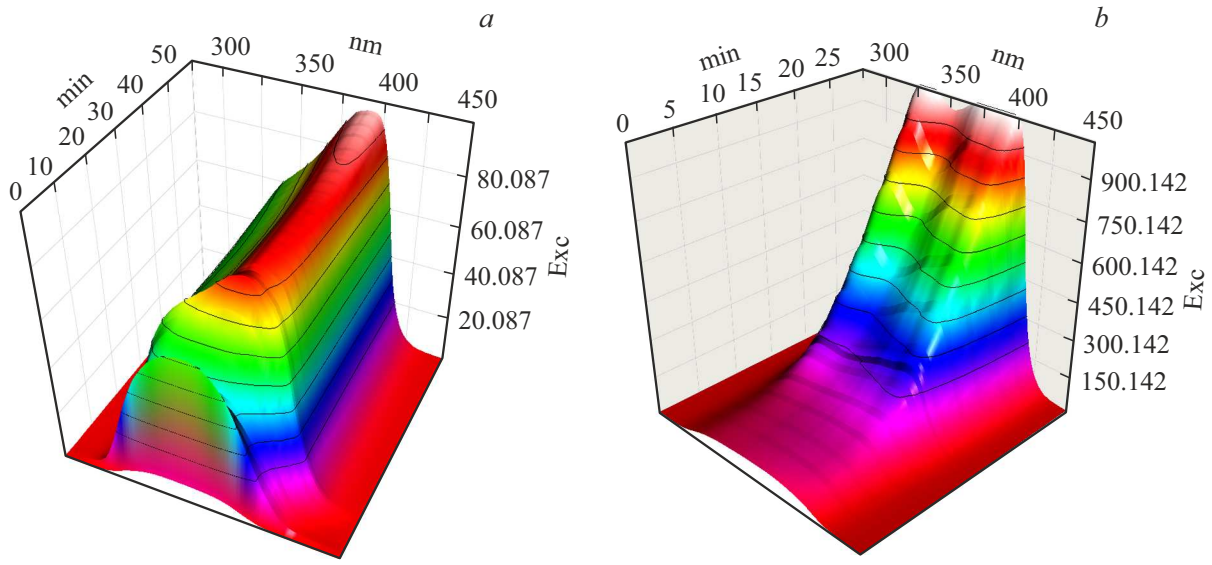

Figure 2. 3D luminescence excitation spectra of the chemosensor exposed to dimethylamine (*a*) and ammonia (*b*) vapors. The y-axis is the intensity in rel. units, the other axes are the time in min and the wavelength in nm.

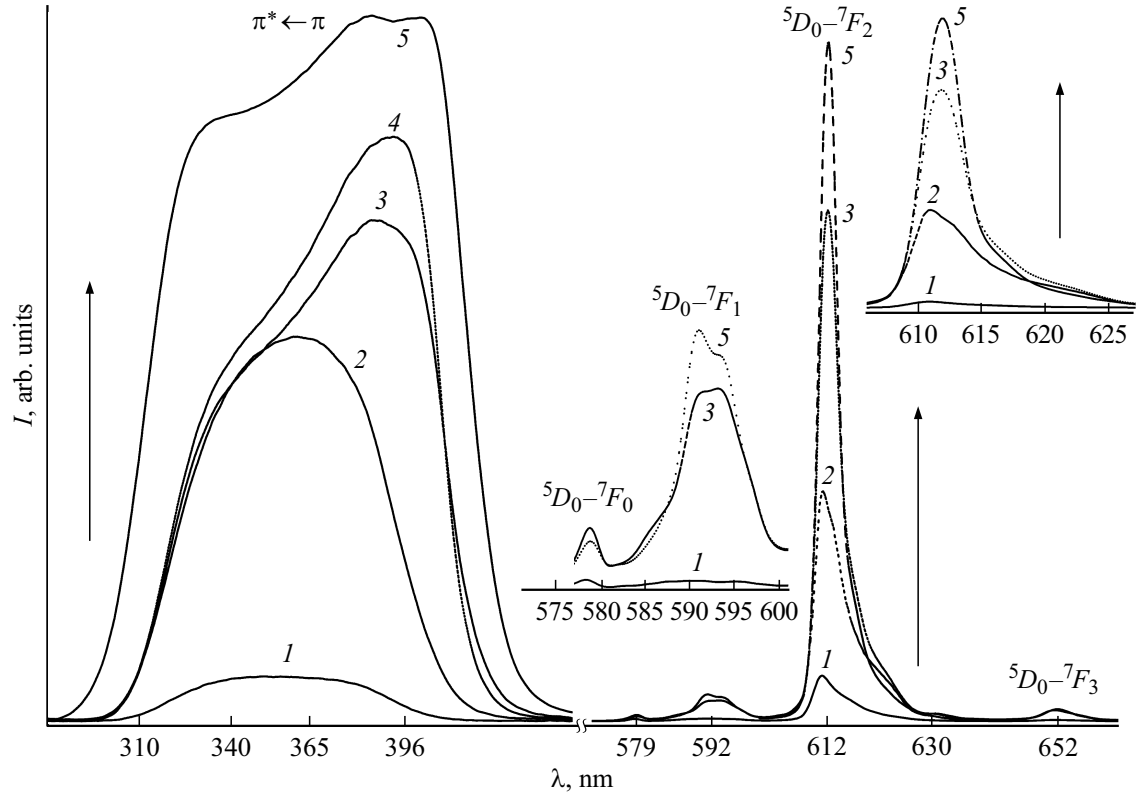

Figure 3. Luminescence excitation and luminescence spectra of a chemosensor exposed to dimethylamine vapors. Luminescence spectra: *1* — 0 s, *2* — 20 s, *3* — 17 min, *5* — 143 min. Luminescence excitation spectra: *1* — 0 s, *2* — 30 s, *3* — 18 min, *4* — 71 min, *5* — 145 min. The insertions show the change in the Stark structure of $^5D_0$–^7F_j ($j = 0, 1, 2$) transitions.

time, under the action of ammonia, a broad diffuse band (355 nm) is transformed to a distinct triplet (330, 380, and 395 nm). These data indicate that, under the action of ammonia molecules, inner coordination sphere of Eu(III) is rearranged and the antenna effect is modulated, i. e. change in the efficiency of energy transfer of ligand-metal electronic excitation.

With further exposure of model chemosensor to ammonia (after 84 min), the luminescence excitation spectra are transformed: the 355 nm band is split into a doublet with

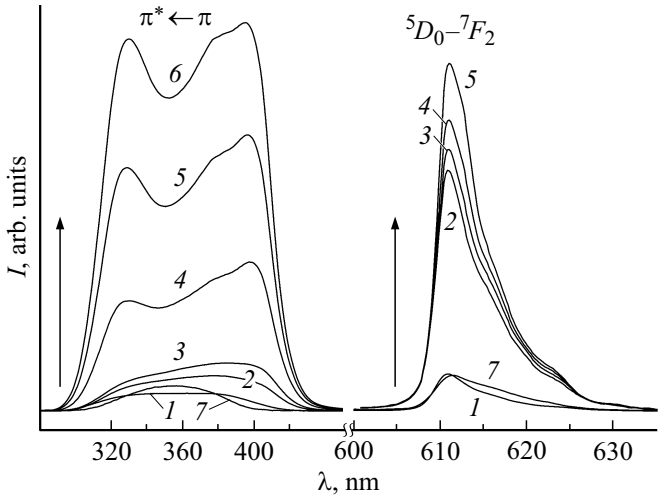

Figure 4. Luminescence excitation and luminescence spectra of a chemosensor exposed to ammonia vapors. Luminescence spectra: *1* — 0, *2* — 20, *3* — 65, *4* — 545, *5* — 880 s. Luminescence excitation spectra: *1* — 0, *2* — 30, *3* — 310, *4* — 980 s, *5* — 21 min, *6* — 25 min, *7* — after purging the chamber and drying the sample.

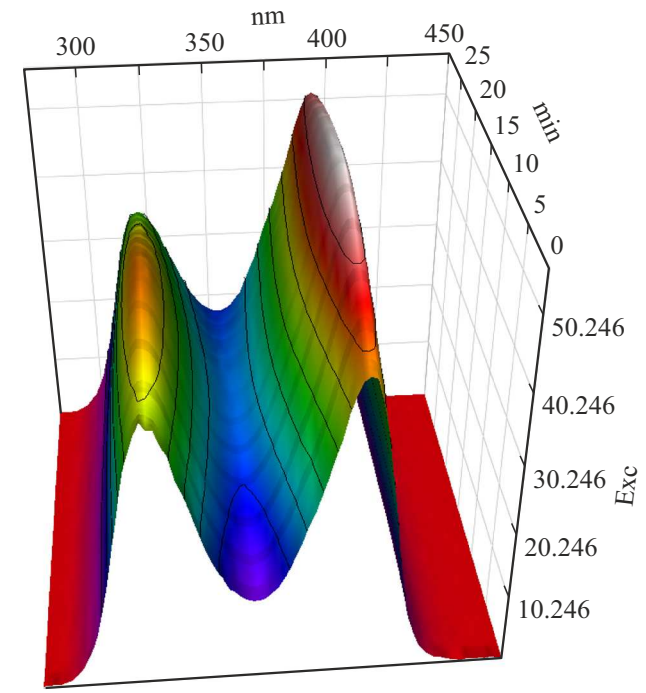

Figure 5. Chemosensor luminescence excitation 3D spectrum under the action of ammonia vapors. The y-axis is the intensity in rel. units, the other axes are the time in min and the wavelength in nm.

maxima 322 and 395 nm (Fig. 5). Increase and reaching a plateau in the luminescence intensity indicates that the quenching action of water vapor reaches a plateau and the processes of luminescence sensitization under the action of ammonia vapors prevail.

An important feature of the $Eu(Dbm)_3 \cdot H_2O$ model chemosensor is the reversibility of the substrate-analyte interaction: when the chemosensor sample is purged and dried, the luminescence intensity is restored (Fig. 4, line *7*), which is confirmed in the articles [24,25].

The data obtained indicate that, in the study of the chemosensory properties of lanthanide complexes, in addition to the analysis of luminescence bands, additional analysis of the luminescence excitation spectra is an effective method for studying the substrate–analyte interaction. It should be noted that a characteristic feature of luminescence excitation spectra evolution is selectivity with respect to the analyte. Indeed, analysis of the experimental data provides strong evidence of the peculiarity of luminescence excitation spectra evolution: under the action of water vapors, a monotonic decrease in the intensity of the bands occurs without changing the band contour. On the other hand, under the action of ammonia and dimethylamine, the intensity of the bands increases and the bands? contours are transformed to a doublet and triplet with different ratios of component intensities. Such selectivity in luminescence excitation spectra evolution can be useful in the analysis of experimental data in the study of the chemosensory properties of lanthanide complexes.

Conclusion

The interaction of Eu(III) tris-dibenzoylmethanate with dimethylamine and ammonia vapors was studied. It was found that when vapors of aqueous solutions of analytes act on Eu(III) tris-dibenzoylmethanate impregnated into the SiO_2 matrix, an optical response is observed in the form of an increase in the Eu(III) luminescence intensity. Changes in the luminescence and luminescence excitation spectra of this sensor are analyzed under both the quenching action of water vapors and the sensitizing action of analyte vapors. The main points recorded in the luminescence excitation spectra, which are important for understanding the processes occurring in the near surrounding of the lanthanide center, are noted.

The data obtained indicate that, in the study of the chemosensory properties of lanthanide complexes, in addition to the analysis of luminescence bands, additional analysis of the luminescence excitation spectra is an effective method for studying the substrate analyte interaction.

The luminescent chemosensor is promising for creating sensors for detecting ammonia and amines in food safety control and environmental monitoring.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M. Venkateswarulu, P. Gaur, R.R. Koner. Sensors and Actuators B: Chem., **210**, 144–148 (2015). DOI: 10.1016/j.snb.2014.12.082

[2] T.W. Bell, N.M. Next. *Optical Biosensors: Present and Future*, ed. by F.S. Ligler and C.A. Rowe Taitt (Elsevier Science B.V., 2002), ch. 11, p. 331–368. DOI: 10.1016/B978-044450974-1/50011-2

[3] A.P. Silva, D.B. Fox, A.J.M. Huxley, T.S. Moody. Coord. Chem. Rev., **205** (1), 41–57 (2000). DOI: 10.1016/S0010-8545(00)00238-1

[4] H.S. Mader, O.S. Wolfbeis. Anal Chem., **82** (12), 5002–5004 (2010). DOI: 10.1021/ac1007283

[5] M. Myers, A. Podolska, C. Heath, M.V. Baker, B. Pejcic. Analyt. Chim. Acta., **819**, 78–81 (2014). DOI: 10.1016/j.aca.2014.02.004

[6] I.A. Ibarra, T.W. Hesterberg, J.S. Chang, J.W. Yoon, B.J. Holliday, S.M. Humphrey. Chem. Commun., **49** (64), 7156–7158 (2013). DOI: 10.1039/C3CC44575E

[7] M.L. Aulsebrook, B. Graham, M.R. Grace, K.L. Tuck. Coord. Chem. Rev., **375**, 191–220 (2018). DOI: 10.1016/j.ccr.2017.11.018

[8] Y. Zhang, B. Li, H. Ma, L. Zhang, Y. Zheng. Biosensors and Bioelectronics, **85**, 287–293 (2016). DOI: 10.1016/j.bios.2016.05.020

[9] H. Weng, B. Yan. Sensors and Actuators B: Chem., **228**, 702–708 (2016). DOI: 10.1016/j.snb.2016.01.101

[10] P.Y. Du, S.Y. Liao, W. Gu, X. Liu. J. Solid State Chem., **244**, 31–34 (2016). DOI: 10.1016/j.jssc.2016.09.011

[11] X. Shen, B. Yan. J. Colloid Interface Science, **451**, 63–68 (2015). DOI: 10.1016/j.jcis.2015.03.039

[12] S. Roy, A. Chakraborty, T.K. Maji. Coord. Chem. Reviews, **273–274**, 139–164 (2014). DOI: 10.1016/j.ccr.2014.03.035

[13] B.V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J.L. Jordá, H. García, D. Ananias, L.D. Carlos, J. Rocha. Angew. Chem. Int. Ed. Engl., 47 (6), 1080–1083 (2008). DOI: 10.1002/anie.200704702

[14] C. Yang, J. Luo, J. Ma, D. Zhu, L. Miao, Y. Zhang, L. Liang, M. Lu. Synth. Met., 162 (13–14), 1097–1106 (2012). DOI: 10.1016/j.synthmet.2012.05.005

[15] B. Timmer, W. Olthuis, A. van den Berg. Sens. Actuators. B, 107 (2), 666–677 (2005). DOI: 10.1016/j.snb.2004.11.054

[16] S.J. Butler, D. Parker. Chem. Soc. Rev., 42 (4), 1652–1666 (2013). DOI: 10.1039/c2cs35144g

[17] V.L. Ermolaev, E.B. Sveshnikova, E.N. Bodunov. Physics-Uspekhi., 39 (3), 261–282 (1996). DOI: 10.1070/PU1996v039n03ABEH000137

[18] E.E. Rumyantseva. *Ekologicheskaya bezopasnost' stroitel'nykh materialov, konstruktsiy i izdeliy* (Universitetskaya kniga, Moskva, 2011) (in Russian).

[19] S.P. Sivkov. Tekhnologii betona, 5–6, 15–17 (2012) (in Russian).

[20] Z. Bai, Y. Dong, Z. Wang, T. Zhu. Environ. Int., 32 (3), 303–311 (2006). DOI: 10.1016/j.envint.2005.06.002

[21] S.A. Lawrence. *Amines: Synthesis, Properties, and Applications* (Cambridge University Press, Cambridge, 2004). DOI: 10.1021/op0501390

[22] A. Pacquit, J. Frisby, D. Diamond, K.T. Lau, A. Farrell, B. Quilty, D. Diamond. Food Chem., 102 (2), 466–470 (2007). DOI: 10.1016/j.foodchem.2006.05.052

[23] G. Meng, L. Shiwu, L. Yuhan, G. Yi, L. Xia, W. Luochao, Q. Anjun, T. Ben Zhong. ACS Sens., 1 (2), 179–184 (2016). DOI: 10.1021/acssensors.5b00182

[24] [N.V. Petrochenkova, A.G. Mirochnik, A.S. Shishov, A.A. Sergeev, S.S. Voznesenskii. Russ. J. Phys. Chem., 88, 158–162 (2014). DOI: 10.1134/S0036024414010191]

[25] A.G. Mirochnik, N.V. Petrochenkova, A.S. Shishov, B.V. Bukvetskii, T.B. Emelina, A.A. Sergeev, S.S. Voznesenskii. Spectrochim. Acta. A, 155, 111–115 (2016). DOI: 10.1016/j.saa.2015.11.004

[26] S.S. Voznesenskiy, A.A. Sergeev, A.G. Mirochnik, A.A. Leonov, N.V. Petrochenkova, A.S. Shishov, T.B. Emelina, Yu.N. Kulchin. Sensors and Actuators. B: Chem., 246, 46–52 (2017). DOI: 10.1016/j.snb.2017.02.034

[27] V.A. Batyreva, V.V. Kozik, V.V. Serebrennikov, G.M. Yakunina. *Sintezy soyedineniy redkozemelnykh elementov*, pod red. V.V. Serebrennikov (Izd-vo Tomskogo un-a, Tomsk, 1983), part 1, p. 133 (in Russian).