Detection of dysprosium (III) in the presence of terbium (III) by using the time-resolved luminescence

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Abstract. The luminescence properties of Tb³⁺ and Dy³⁺ complexes containing newly synthesized pyrazole-5-carboxylic acids have been studied. It was established that lifetimes (τ) of ⁴F₉/₂ emission of Dy³⁺ ion in these complexes changes from <3 to 6 µs, while those ⁵D₄ emission of Tb³⁺ ion characterizes by τ=435-910 µs. The principal possibility of Dy³⁺ detection in the presence Tb³⁺ by means of time-resolved luminescence was shown for the first time. It was proved by the determination of Dy³⁺ in luminescent materials doped by both Tb³⁺ and Dy³⁺, simultaneously.

1. Introduction
Lanthanide compounds due to their unique luminescence properties are widely in variety of bioanalytical assays, in diagnostic, research, drug discovery, phosphors, for displays and lighting devices (light-emitting diodes), etc. are applied [1-5]. The absorption energy in lanthanide complexes transfers by intramolecular non-radiative energy transfer processes from the singlet to the triplet state of ligand and then to the emission level of the lanthanide ion (Ln³⁺) which emits characteristic long or short lifetimes luminescence.

The luminescent analysis provides a high sensitivity and in some cases – selectivity of lanthanide determination. However, determination Ln⁻⁵⁺ in pair of neighbor elements as Sm-Eu, Tb-Dy is the most complicated task. Analytical bands of these lanthanides in spectra are shifted from each other by on ≤30 nm, what limits determination of the one element in the presence of other in numerous quantities.

It is known that determination of a microamounts of Sm³⁺ (3×10⁻⁵%) in Eu₂O₃ and Eu³⁺ (1×10⁻⁵%) in Sm₂O₃ masking [6] and sorption [7] were used respectively. The same approaches for determination of Dy³⁺ in Tb³⁺ compounds are inefficient in the luminescent analysis of any systems, including solids, because two Tb³⁺ bands (λₘₚ₅=545 and 585 nm) are situated near Dy³⁺ band (λₘₚ₅=574 nm) as well as more weak dysprosium luminescence intensity at the same time.

The time-resolved luminescence employing long-lifetime luminescence of lanthanide, chelate labels have been routinely applied in diagnostics for two decades [8-11]. Laser-exited time-resolved fluorimetry was used for the determination of both Sm³⁺ and Eu³⁺ with absolute detection limit 3·10⁻¹¹ µg/ml and 5·10⁻¹³ µg/ml respectively in complexes with 2-naphthoyltrifluoroacetone and trioctylphosphine oxide is used as a markers for biological molecules [12]. Threat in all cases it was used to eliminate short-lived fluorescence caused by, e.g., an excess of fluorescent ligands, contamination of sample constituents, etc. Under the same conditions the lifetime fluorescence of Eu³⁺, Tb³⁺ and Sm³⁺, for example, in their chelate complexes is 618, 695 and 89 µs, whereas the lifetime of Dy³⁺ chelates was not determined due to short-lifetimes [9]. Detachment possibility of short-lifetime component of weak luminescent Ln (Sm³⁺, Dy⁵⁺) on
the background of the long-lifetime intensive luminescent Ln (Tb\(^{3+}\), Eu\(^{3+}\)) especially in such pair neighbor elements as Eu-Sm and Tb-Dy were not studied.

In this research the methods of the Dy\(^{3+}\) determination through the detachment of its short-lifetime luminescence on the background of Tb\(^{3+}\) long-lifetime luminescence and at the dysprosium determination in luminescent materials doped by both these elements were elaborated.

2. Experimental

2.1. Reagents

Pyrazol-5-carboxylic acids were synthesized according to the known procedures [13, 14]. Individuality and purity of these compounds were checked by methods of IR-, HMR-spectroscopy, mass-spectrometry and elemental analysis. The sodium salts of these acids were used in experiments.

Terbium and dysprosium stock solutions of \(1 \cdot 10^{-3} \text{M}\) were prepared by dissolving a known amount of these oxides (Aldrich) in dilute (1:1) hydrochloric acid. Standard solutions were prepared by proper dilution. The pH 3.5 of solution was adjusted by using the buffer prepared from sodium hydroxide and acetic acid in various concentrations.

2.2. Apparatus

The absorption spectra were recorded on an Lambda-9 UV/VIS/NIR (Perkin-Elmer) spectrophotometer. Luminescence measurements were carried out with SDL-1 spectrophuorimeter (Leningrad Optic-mechanical Association, St. Petersburg, Russia) equipped with a DRSh-250 mercury lamp and UFS-2 light filter. Luminescence was excited at 254 nm. The measurements of excitation and time-resolved luminescence, spectra, decay times and analytical determination of dysprosium in luminescent materials were carried out with Fluorat-02 panorama spectrofluorimeter (Lumex, St. Petersburg, Russia). Luminescence was excited by an impulse xenon lamp (\(\tau=0.5 \mu\text{s}\)). Luminescence spectra were recorded within the region 450-600 nm.

The energy values of ligands triplet T\(_1\)-levels were determined from phosphorescence spectra of their complexes with Gd\(^{3+}\) at 77 K.

The luminescence quantum yields (\(\phi\)) of the terbium and dysprosium complexes (\(\lambda_{\text{em}}=295\text{ nm}\)) were calculated by method described in [15] using a quinine bisulphate (\(\phi=0.546\) in 0.5 mol H\(_2\text{SO}_4\)) as a standard.

3. Results and discussions

Absorption spectra of the pyrazol-5-carboxylic acids and their complexes with Tb\(^{3+}\) and Dy\(^{3+}\) in water solutions are characterized by the presence of strong bands in the UV region (210-320 nm). Extinction coefficients are \(\varepsilon=(2.5-6.8) \times 10^4 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}\). The luminescence intensity of Tb\(^{3+}\) and Dy\(^{3+}\) pyrazolcarboxylates was observed at the same pH of solutions. Characteristics of all complexes are given in Table 1.

| Ligands | Characteristics of complexes |
|---------|-----------------------------|
| Structural formula and Abbreviation | \(E_T, \text{cm}^{-1}\) | pH | \(\varepsilon, 10^4\) | \(\lambda_{\text{ex}}, \text{nm}\) | Tb | Dy |
| | | | | | \(\lambda_{\text{em}}=544 \text{nm}\) | \(\lambda_{\text{em}}=574 \text{nm}\) |
| BPA | 23000 | 7.0 | 2.5 | 237 | 140 | 555 | 2.7 | 5 |
| PhPA | 21000 | 4.0 | 5.3 | 268 | 150 | 450 | 3.2 | 4 |
| CPhPA | 21150 | 7.0 | 6.1 | 278 | 530 | 650 | 9.8 | 5 |
| BOPA | 22200 | 3.5 | 6.8 | 295 | 1220 | 910 | 27.3 | 6 |
In accordance with energy of the ligand triplet levels (21.000-23.250 cm⁻¹) transfer of excitation energy from ligand to Tb³⁺ and Dy³⁺ emitting levels is possible principally (Figure 1).

The excitation spectrum monitored at 544 nm for the dilute solution of Tb(BOPA)₃, for example, consists of several overlapping bands within range 220-360 nm with maxima at ~245 and 295 nm (Figure 2, a). The emission spectra of this complex has a four main bands at 490 nm (³D₄ → ⁷F₆), 544 nm (³D₄ → ⁷F₅), 586 nm (³D₄ → ⁷F₄) and 622 nm (³D₄ → ⁷F₃). Electro-dipole transition ³D₄ → ⁷F₃ is the strongest. These bands were observed in emission spectra of Tb³⁺ complexes with all ligands.

The emission spectra of Dy³⁺ pyrazolcarboxylates consist of two intense emission bands in visible region at 480 nm (⁴F₉/2 → ⁶H₁₅/₂), 574 nm (⁴F₉/2 → ⁶H₁₃/₂) and a very weak band in IR-region at 1007 nm (⁴F₉/2 → ⁶H₃/₂). As shown in Figure 3, the electro-dipole transition ⁴F₉/2 → ⁶H₁₃/₂ is the strongest.
The most intense and long-lifetimes luminescence of Tb\(^{3+}\) (as well as Dy\(^{3+}\)) is observed in their complexes with BOPA (3-(6-benzodioxanyl)-pyrazol-5-carboxylic acid; see Table 1). The values of the lifetimes (\(\tau\)) and relative quantum yields (\(\phi\)) for the complexes Tb\(^{3+}\) and Dy\(^{3+}\) with BOPA in three different solvents are given in Table 2.

Table 2. Quantum yields and lifetimes of complexes Tb\(^{3+}\) and Dy\(^{3+}\) with BOPA in the presence of different solvents (AN – acetonitrile, DMSO – dimethylsulfoxide).

| Solvents        | \(\tau\), µs | \(\phi\), % | Solvents        | \(\tau\), µs | \(\phi\), % |
|-----------------|--------------|-------------|-----------------|--------------|-------------|
| \(\text{H}_2\text{O}\) | 910±9        | 5.8±0.6     | \(\text{AN} (80\ % \text{vol.})\) | 950±10       | 6.0±0.6     |
| Tb-BOPA         | 1820±18      | 8.7±0.9     | DMSO (80 % vol.) | 15±1.5       | 0.40±0.04   |
| Dy-BOPA         | 6±0.6        | 0.20±0.02   |                 |              |             |

As shown in Table 2, the presence DMSO leads to the increase of \(\tau\) and \(\phi\) of complexes Tb\(^{3+}\) and Dy\(^{3+}\) with BOPA. It is evident that this is due to effective removal water molecules from inner coordination sphere of the complexes. However, in all cases \(\tau\) for Tb\(^{3+}\) exceeds \(\tau\) for Dy\(^{3+}\) in 120-150 times.

Fast non-radiative deactivation of Dy\(^{3+}\) ion excited is caused by a small energetic gap between the excited level \(^{5}F_{4}/2\) and sublevels of basic term \(^{1}H_{3/2}, 5/2, 7/2\). At the detachment of short-lifetime luminescence of Dy\(^{3+}\) (Figure 4) the influence of Tb\(^{3+}\) luminescence is not excluded completely because the long-lifetime component of Tb\(^{3+}\) luminescence passed in «time-gate» too (Figure 4). It was found that using of time-gate 0.05-10 µs allows the Dy\(^{3+}\) luminescence registration in water solution at 5-fold excess of Tb\(^{3+}\). However, the Tb\(^{3+}\) excess may be increased up to 10-fold at suppress of energy losses on OH-oscillators (water molecules) in the inner coordination sphere in the presence DMSO (80% vol.).

Without using the time-resolved luminescence technique it was possible to determine Dy\(^{3+}\) in the presence of Tb\(^{3+}\) only at ratio Dy:Tb=1:0.1.

The advantages of time-resolved luminescence were demonstrated on spectra of Tb\(^{3+}\) and Dy\(^{3+}\) complexes with BOPA in analysis of luminescent materials, doped Tb(1.5%) and Dy(0.5-5.0%) (Figure 5). These spectra shows that the Dy\(^{3+}\) determination is possible only by using the time-resolved luminescence technique because the luminescence band of Tb\(^{3+}\) (\(\lambda_{\text{max}}=586\ nm\)) not overlap to luminescence band of Dy\(^{3+}\) (\(\lambda_{\text{max}}=574\ nm\)).
Figure 5. Emission spectra of a mixture of Tb$^{3+}$ and Dy$^{3+}$-BOPA complexes obtained from a dilute HCl solution of Sc$_{0.980}$Tb$_{0.015}$D$_{0.005}$BO$_3$ sample. The spectra were recorded for two different time intervals after pulse excitation: 1 – between 0.05-10 µs; 2 – 0.05-1000 µs.

The results of Dy$^{3+}$ determination in luminescent materials by proposed method are given in Table 3. As can be seen the found contents of Dy$^{3+}$ are in a good accordance with those chosen in the synthesis.

Table 3. The results of Dy$^{3+}$ determination in luminescent materials by using the time-resolved luminescence (n=5, P=0.95)

| Sample                | Content Dy, % | Found Dy, %  | RSD   |
|-----------------------|---------------|--------------|-------|
| Sc$_{0.935}$Tb$_{0.015}$Dy$_{0.05}$BO$_3$ | 5.00          | 4.94±0.08    | 0.013 |
| Sc$_{0.975}$Tb$_{0.015}$Dy$_{0.01}$BO$_3$ | 1.00          | 1.02±0.06    | 0.047 |
| Sc$_{0.98}$Tb$_{0.015}$Dy$_{0.005}$BO$_3$ | 0.50          | 0.46±0.03    | 0.054 |

4. Conclusions

On the base of investigation of time-resolved luminescence spectra of Tb$^{3+}$ and Dy$^{3+}$ complexes with 3-(6-benzodioxanyl)-pyrazol-5-carboxylic acid (BOPA) for the first time the possibility of the detachment short-lifetime luminescence for the Dy$^{3+}$ determination in the presence of Tb$^{3+}$ was established. Thus, it is possible to determine Dy$^{3+}$ in luminescent materials with the use of its complex compounds despite of almost complete overlap of Tb-band (586 nm) and analytical Dy-band (574 nm).

References

1. Soukka T, Kuningas K, Rantanen T, Haaslah V and Lorgen T 2005 *J. Fluoresc.* **15** 513
2. Hemmila I and Laitala V 2005 *J. Fluoresc.* **15** 529
3. Tanabe S 2002 C R Chimie **5** 815
4. Bunzli J-C G and Piquet C 2005 *Chem. Soc. Rev.* **34** 1048
5. Marchetti F, Pettinari C and Pettinari R 2005 *Coord. Chem. Rev.* **249** 2909
6. Meshkova S B and Rusakova N V 1990 *Zh. Anal. Khim.* **45** 1917
7. Meshkova S B, Topilova Z M, Nazarenko N A, Litvinenko A V and Efryushina N P 2004 *Zh. Anal. Khim.* **59** 280
8. Valeur B and Brochon J-C (Eds.) 2001 *New Trends in Fluorescence Spectroscopy* (Berlin: Springer)
9. Huntinen P, Kivela M, Kuronen O, Hagren V, Takalo H, Tenhu H, Lovgren T and Harma H 2005 *Anal. Chem.* **77** 2643
10. Bright F V and Munson C A 2003 *Anal. Chim. Acta* **500** 71
11. Romanovskaya G I 1993 *Zh. Anal. Khim.* **48** 198
12. Morin M, Bador R, Dechaud H 1989 *Anal. Chim. Acta* **219** 67
13. Elguero J, Guiraud G, Jacquer R 1966 *Bull. Soc. Chim.* France №2 619
14. Bulow C 1904 *Ber. Dtsch. Chem. Ges.* **37** 2198
15. Terai T, Kikuchi K, Iwasa S, Kawabe T, Hirata Y, Urano Y, Nagano T 2006 *J. Am. Chem. Soc.* **128** 6938