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Sensitization of the 4*f*-Luminescence of Terbium with Copper Ions and Its Analytical Application

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Abstract—The intense sensitization of terbium luminescence with copper(II) ions was observed in the Tb–Cu mixed-metal complex of 1.5-bis(2-hydrazinocarbophenoxy)-3-oxapentane (HCPhO) with the ratio Tb : Cu : HCPhO = 1 : 1 : 1. Other *d*-block metals produced no sensitizing effect. The effect observed was used for the luminescence determination of trace copper in the presence of 1000-fold amounts of Mn(II), Fe(III), Co(II), Ni(II), Zn(II), and Cd(II). The accuracy of determining copper was verified by the analysis of Certified Reference Materials of zinc- and nickel-based alloys.

Luminescence analysis is characterized by the high sensitivity and selectivity of the determination of a great number of elements. For detecting copper, it is mainly used in the atomic fluorescence version [1]. However, it is known that Cu(I) ions can be directly determined by the luminescence of solutions of their complexes with pyridine and other organic bases and halide ions [2] and indirectly determined by quenching the luminescence of ligands [3–5] and by the catalytic effect of copper on the oxidation of morin or ninhydrin with hydrogen peroxide [6]. The fluorescent sensor systems based on Cu(II)–protein [7] and Cu(II)–macrocyclic ligand [8] complexes were also proposed for the determination of copper. Silica gel modified with mercapto groups to which Cu(II) ions were bonded was used for the determination of copper in water [9]; Cu(II) was first reduced to Cu(I), and then the intense yellow–orange luminescence of Cu(I) with a maximum at 585 nm was measured. By freezing the adsorbates to 77 K, the authors of [9] could achieve a detection limit for copper of 0.08 μg per 0.1 g of the adsorbent.

Papers devoted to the determination of copper based on its sensitizing effect on the 4*f*-luminescence of lanthanides are lacking. On the contrary, it is known that, of *d*-block metals, copper and iron are the strongest quenchers of the luminescence of lanthanide ions in the solutions of their complexes of different organic ligands [10], including mixed-metal *f–d* complexes [11, 12]. When studying the *f–d* complexes of 1,5-bis-(2R-phenoxy)-3-oxapentane derivatives, we observed the intense sensitization of Eu(III) and Tb(III) luminescence with copper ions [13, 14]. The enhancement of terbium luminescence in its complex with 1,10-bis(2'-carboxyphenyl)-1,4,7,10-tetraoxadecane in the solution of an AgCl sol was used for determining silver by the sensitized Tb luminescence [15].

The goal of this work was to find the conditions under which the sensitization of the 4*f*-luminescence of terbium(III) in a Tb–Cu mixed-metal complex attains a maximum and study the possibilities of using a new analytical form in determining trace copper in the presence of other *d*-block metal ions.

EXPERIMENTAL

In our work, we used the following derivatives of 1,5-bis-[2R-4(5)R'-phenoxy]-3-oxapentane of the general formula
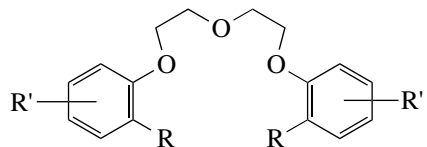
where R = NH₂, R' = H (1,5-bis-(2-aminophenoxy)-3-oxapentane, APhO); R = COOH, R' = H (1,5-bis-[2-(hydroxycarbonyl)phenoxy]-3-oxapentane, HOC-PhO); R = CONHNH₂, R' = H (1,5-bis-[2(hydrazinocarbonyl)phenoxy]-3-oxapentane, HCPhO); R = OH, R' = C(CH₃)₃ (1,5-bis-[2hydroxy-4(5)-*tert*-butylphenoxy]-3-oxapentane, HBPhO).

The APhO and HOCPhO reagents were synthesized by the reaction of 2-acetaminophenol or methylsalicylate, respectively, with diethylene glycol ditosylate in the presence of anhydrous K₂CO₃ (DMF, 80°C, 7 h) followed by the hydrolysis of the intermediate acetyl derivative of APhO and dimethylate of HOCPhO. HCPhO was obtained by treating HOCPhO with excess hydrazine hydrate (105°C, 5 h). HBPhO was synthesized by the reaction of 4-*tert*-butylpyrocatechol with chlorex in the presence of anhydrous Na₂CO₃ (glycerol, 150°C, 5 h).

Table 1. Luminescence intensity of terbium complexes (I_1) in the absence and (I_2) in the presence of copper(II) ions

Reagent	I, rel. units		I_2/I_1
	I_1	I_2	
APhO	7	4	0.57
HOCPhO	45	40	0.89
HCPhO	9	269	29.89
HBPhO	9	5	0.56

Acetonitrile solutions (1×10^{-2} M) of APhO, HOCPhO, HCPhO, and HBPhO were prepared from accurately weighed samples of their preparations. Their absorbances were maximum in the range from 260 to 320 nm. An aqueous 0.1 M TbCl$_3$ stock solution was prepared by dissolving terbium oxide (99.99% purity) in HCl solution, an aqueous 0.1 M solution of copper chloride was prepared from CuCl$_2 \cdot$ 2H$_2$O (analytical grade). The working solutions were obtained by diluting the stock solutions.

Single- and mixed-metal complexes were prepared by mixing metal chloride solutions with a reagent solution at the optimum pH that was adjusted by adding corresponding acetate buffer solutions. The water-to-acetonitrile ratio in the test solutions was 9 : 1. The pHs of solutions were controlled using an OP-211 pH-meter (Hungary). Absorption spectra were measured on a Lambda-9 UV/VIS/NIR Perkin–Elmer spectrophotometer, and luminescence spectra were recorded using an SDL-1 diffraction spectrometer. The luminescence of

complexes was excited with a DRSh-250 mercury lamp, and UV radiation was isolated with an UFS-2 light filter. The X-ray diffraction analysis of complexes was performed on a DRON instrument using Ni-filtered CuK_α radiation.

The compositions of single-metal (Tb) and mixed-metal (Tb–Cu) complexes and the effect of the pH of the solution were studied by measuring the luminescence of the most intense terbium line at 545 nm (supersensitive $^5D_4 \longrightarrow {}^7F_5$ transition) in spectra recorded from 530 to 570 nm. The entire spectrum of terbium luminescence was taken in the range 400 to 700 nm, the luminescence of the copper complex was recorded in the same spectral range.

RESULTS AND DISCUSSION

Table 1 presents luminescence intensities (I) of solutions of terbium complexes of test reagents before (I_1) and after (I_2) the addition of Cu(II) and the I_2/I_1 value, which characterizes the effect of copper on terbium luminescence. It follows from the data presented Table 1 that copper(II) added to the solutions of terbium APhO and HBPhO complexes quenched the 4f-luminescence almost by one half. Copper(II) ions quenched the luminescence of terbium in the Tb–HOCPhO complex more weakly. The sensitizing effect of copper(II) ions on terbium luminescence was observed only for its complex with HCPhO.

As follows from Fig. 1, the optimum pH for observing the luminescence of terbium and copper in their single-metal HCPhO complexes was 3 and 6, respectively. The sensitizing effect of copper(II) ions on the luminescence of terbium in its HCPhO complex was observed in the rather narrow pH range (5.7–6.5). At these pH values, the background emission of HCPhO in the visible spectral region is negligible.

The maximum luminescence intensity was reached within 30 min after mixing the components; it remained unchanged for 24 h. It was found by the luminescence method that the ratios of components in single-metal terbium and copper HCPhO complexes were 1 : 1. The formation of a mixed-metal Tb–Cu–HCPhO complex and the stoichiometry of its components was studied by adding variable amounts of a CuCl$_2$ solution to the solution of the Tb–HCPhO (1 : 1) complex. When an equilibrium was attained, the luminescence intensity of the terbium line with λ_{max} = 545 nm was measured. As can be seen in Fig. 2, the ratio of the components in the resulting Tb : Cu : HCPhO complex was 1 : 1 : 1.

A comparison of the times of the formation of the mixed-metal complex (Fig. 3) upon the simultaneous mixing of all the components (curve *1*) and upon the mixing of equimolar amounts of single-metal complexes (curve *2*) indicates that the Tb–Cu–HCPhO complex was formed regardless of the way of its preparation. Up to fivefold amounts of the reagent quenched
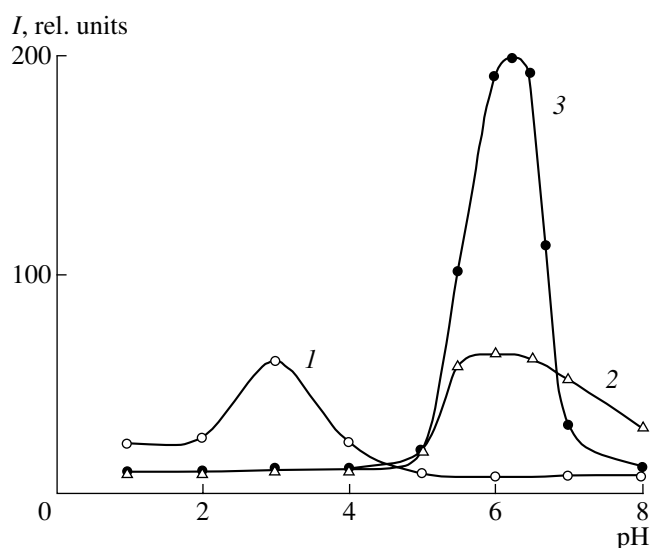

Fig. 1. Luminescence intensity of (*1*) Tb–HCPhO and (*2*) Cu–HCPhO single-metal and (*3*) Tb–Cu–HCPhO mixed-metal complexes as functions of the pH of solutions ($c_{Tb, Cu, and HCPhO} = 1 \times 10^{-4}$ M; $\lambda_{Tb–HCPhO, Tb–Cu–HCPhO}$ = 545 nm; $\lambda_{Cu–HCPhO}$ = 440 nm).
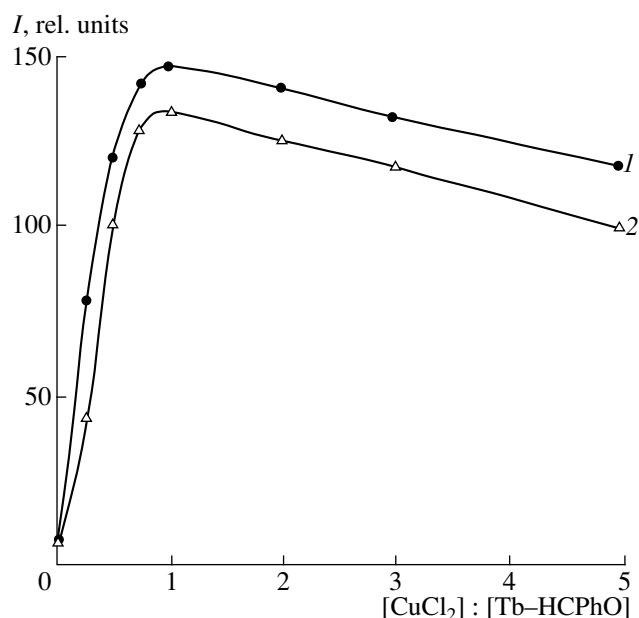
Fig. 2. Luminescence intensity of terbium as a function of the [CuCl$_2$] : [Tb-HCPhO] ratio at pH 6.3 and c_{Tb}–HCPhO of (*1*) 1×10^{-4} and (*2*) 2×10^{-4} M.
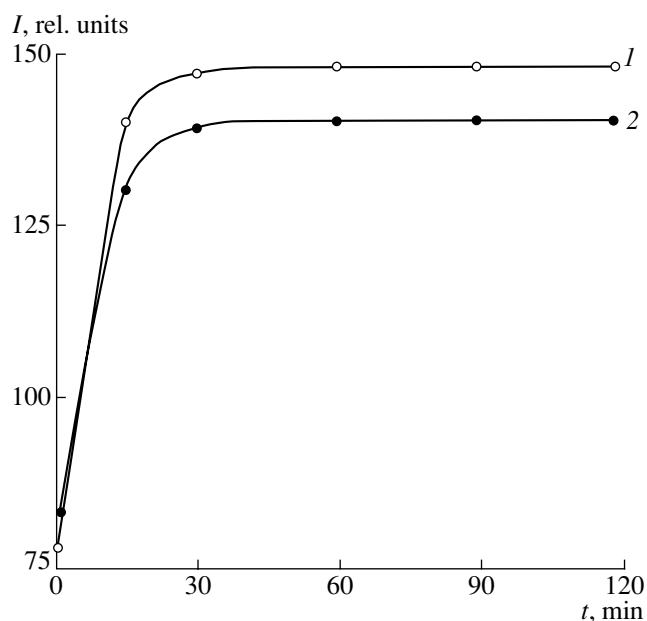

Fig. 3. Time dependence of the luminescence intensity of the Tb–Cu–HCPhO mixed-metal complex obtained (*1*) by the simultaneous mixing of the components (1×10^{-4} M Tb + 1×10^{-4} M Cu + 2×10^{-4} M HCPhO) and (*2*) by the mixing equal volumes of 1×10^{-4} M solutions of single-metal Tb–HCPhO and Cu–HCPhO complexes.

neither the luminescence of the single-metal complexes nor the luminescence of the mixed-metal complex.

Figure 4 presents the luminescence spectra of Tb–HCPhO (spectra *1*, *1'*) and Cu–HCPhO (spectra *2*, *2'*) single-metal complexes and of the Tb–Cu–HCPhO (spectra *3*, *3'*) mixed-metal complex prepared at two pH values, pH 3 (Fig. 4a) and pH 6.3 (Fig. 4b). The first value of pH was optimum for the formation of the Tb–HCPhO complex and pH 6 was optimum for the formation of both Cu–HCPhO complex and Tb–Cu–HCPhO mixed-metal complex. The component concentrations and the conditions of spectra measurement were identical. A comparison of the spectra shows that, at pH 3 (Fig. 4a), when the formation of the Cu–HCPhO complex was hindered, copper(II) ions quenched the luminescence of terbium as they usually did, reducing its intensity by a factor of 2.4 (spectra *1* and *3*). At the same time, the conditions for the formation of the Cu–HCPhO complex and the Tb–Cu–HCPhO mixed-metal complex (pH 6.3) turned out to be optimum for the drastic enhancement of the intensity of Tb luminescence due to its sensitization. In the spectra of the Tb–HCPhO complex (spectra *1* and *1'*), the lines at 490 and 545 nm, which corresponded to the $^5D_4 \longrightarrow {}^7F_6$ and $^5D_4 \longrightarrow {}^7F_5$ supersensitive transitions, respectively, and weak lines at 595 and 622 nm (spectrum *1'*), which corresponded to the transitions from the $^5D_4$ emitting level to the ground $^7F_{4,3}$ sublevels, were observed. The molecular band of the Cu–HCPhO complex luminescence (spectra *2* and *2'*) in the near visible spectral region is characterized by a maximum at 440 nm. In the spectrum of the compound obtained by the simulta-
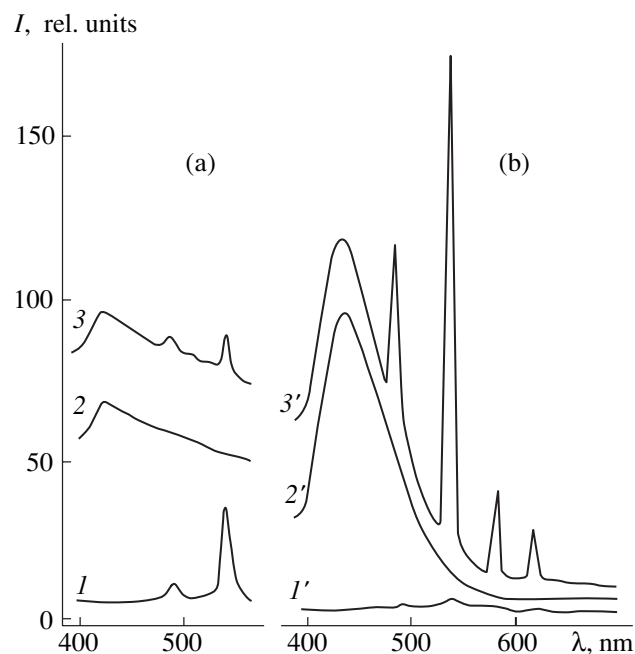

Fig. 4. Luminescence spectra of the solutions of (*1, 1'*) Tb–HCPhO and (*2, 2'*) Cu–HCPhO single-metal complexes and (*3, 3'*) Tb–Cu–HCPhO mixed-metal complex at (a) pH 3 and (b) 6.3 ($c_{Tb-Cu-HCPhO} = 1 \times 10^{-4}$ M).

neous complexation of terbium, copper, and HCPhO (pH 6.3) (spectrum *3'*), the bands characteristic for both complexing ions were observed. The intensities of all

Table 2. Determination of 0.2 µg copper in 10 mL of model solutions (the amount of each element was 20 µg) ($n = 5$; $P = 0.95$)

Model solution	Found Cu, µg	RSD, %
Mn(II), Fe(III), Co(II), Ni(II), Zn(II)	0.20 ± 0.01	6
Ni(II), Zn(II), Cd(II), Fe(III), Pb(II)	0.22 ± 0.01	4
Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), Pb(II)	0.21 ± 0.02	7

lines corresponding to the *f–f*-luminescence of the terbium(III) ion sharply increased. Such efficient sensitization of terbium(III) luminescence with copper(II) ions may be due to their intramolecular rather than intermolecular interaction, which indirectly confirms the formation of the mixed-metal complex in which terbium is surrounded by oxygen atoms, whereas nitrogen atoms of hydrazine fragments are coordinated to copper. The formation of terbium and copper single-metal and mixed-metal complexes with HCPhO is supported by the results of X-ray diffraction analysis.

Thousandfold amounts of Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), and Hg(II) did not sensitize the luminescence of terbium and did not interfere with the determination of copper under the conditions of the formation of Tb–Cu–HCPhO mixed-metal complex.

We studied the effect of organic solvents (methanol, ethanol, acetone, acetonitrile, dioxan, DMF, and DMSO) on the intensity of terbium luminescence in its mixed-metal complex. It was demonstrated that the solvents under study with the exception of acetone enhanced the luminescence of terbium by several and more (DMSO) times in the concentration range from 5 to 70 vol %. For the majority of solvents, the optimum concentrations at which the maximum *I* was observed were 30–40 vol %. This maximum was due to the displacement of water molecules quenching the luminescence of lanthanide ions from the first coordination sphere of the complex.

The possibility of determining trace copper by the copper-sensitized luminescence of Tb in the Tb–Cu–HCPhO mixed-metal complex was studied. We ana-

lyzed model mixtures in which copper was determined by the "added–found" method (Table 2). The Tb–HCPhO complex served as a reagent. The calibration graph was linear in the copper concentration range from 0.01 to 0.5 µg/mL.

Determination procedure. A 1-mL portion of a model mixture of metals (100–150 µg) was placed in each of three test tubes. Then, 0.2 mL of a copper solution containing 1 µg/mL Cu denoted as "added" was added to the first test tube, 0.4 mL of the same solution denoted as ("added" + addition I) was added to the second test tube, and 0.6 mL of the same solution denoted as ("added" + addition II) was added to the third test tube. A 1-mL portion of a sodium acetate buffer solution (pH 6.3), 1 mL of 1×10^{-3} M solution of the Tb–HCPhO complex, 4 mL of DMSO, and twice-distilled water to 10 mL of the total volume were added to each of the three test tubes. The contents of test tubes were stirred, the pH of the solutions was maintained at 6.2–6.3 using the pH-meter. Within 30 min, the solutions were transferred in turn to a quartz cell, and the intensity of terbium luminescence was measured in the region of 530–570 nm. The added amount of copper was calculated by the formula used in the standard addition method [10].

The results of determining copper were verified by the analysis of certified reference materials (GSOs) of zinc- and nickel-base alloys. Portions of GSOs of Zn- and Ni-base alloys were dissolved in HCl and HNO_3, respectively, and the solutions were evaporated to dryness. Stock solutions containing 10 mg/mL of Zn-base and Ni-base alloys were obtained by dissolving the corresponding dry residues in twice-distilled water in 250-mL volumetric flasks. The working solutions contained 1 mg/mL of the alloys. The concentration of copper in these samples was determined as described above. The results of determining copper are summarized in Table 3.

The found and certified copper concentrations are in good agreement. The relative standard deviation of the results of determination was no worse than 5%. The determination limit for copper in the developed procedure was 0.01 µg/mL.

Table 3. Determination of copper in certified reference materials of zinc- and nickel-base alloys ($n = 5$; $P = 0.95$)

Sample (weight fractions of impurities, %)	Certified concentration of copper, %	Found Cu, %	RSD, %
Zn GSO M92 no. 921 (Sn 0.061; Al 3.92; Cd 0.010; Fe 0.012; Pb 0.018)	0.063 ± 0.005	0.063 ± 0.003	5
Zn GSO M45 no. 454 (Sn 0.004; Cd 0.022; Fe 0.015; Pb 0.044)	0.033 ± 0.004	0.032 ± 0.002	3
Ni GSO 3144–84 (Bi 0.006; Sb 0.0001; Sn 0.003; Fe 0.19; Pb 0.005)	0.158 ± 0.007	0.155 ± 0.006	4
Ni GSO 3143–85 (Bi 0.005; Sb 0.0002; Sn 0.004; Cd 0.0005; Fe 0.126; Si 0.19)	0.119 ± 0.003	0.123 ± 0.002	3

ACKNOWLEDGMENTS

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