Spectrofluorimetric Determination of Trace Terbium(III) Using 2,6-Bis-(1'-phenyl-3'-methyl-5'-oxopyrazole-4') Pyridinediacyl and N-Cetylpyridium Bromide

Jin Zhang GAO*, Qi Liang DENG, Wu YANG, Jing Guo HOU,
Bao Wei ZHAO, Jing Wan KANG

Department of Chemistry, Northwest Normal University, Lanzhou 730070

Abstract: A new spectrofluorimetric method for determination of trace terbium based on its reaction with 2,6-bis-(1'-phenyl-3'-methyl-5'-oxopyrazole-4') pyridinediacyl (H_2PMBPP) and N-cetylpyridium bromide (CPB), at an apparent pH=5.0 provided by a hexamethylenetetramine (5% w/w)-hydrochloric acid buffer, is proposed. The calibration graph is linear in the range from 1.43×10^{-5} to 0.1589 μg/ml.

Keywords: Spectrofluorimetric, terbium determination, fluorimetry, 2,6-bis-(1'-phenyl-3'-methyl-5'-oxopyrazole-4') pyridinediacyl.

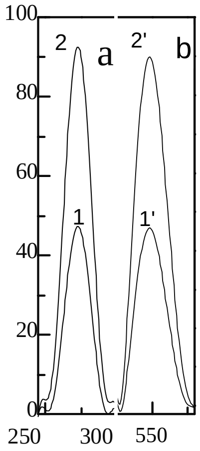
The chemical properties of the rare earth elements are very similar, consequently, it is difficult to find specific reactions for individual ions, especially in their mixtures. Due to higher sensitivity and selectivity, fluorescence analysis of rare earth elements have been an area of active study in recent years.

Bis (4-acylpyrazol-5-one) derivatives have been widely applied in laboratory or industrial scale extraction of metal ions[1-4]. But these compounds have been little utilized as potential luminescent label reagents. In the present paper, the fluorescence properties of the complex of Tb (III)-H_2PMBPP-CPB have been investigated. The spectrofluorimetric determination of trace amounts of Tb (III) based on the above system was carried out.

Apparent fluorescence excitation and emission spectra were obtained at room temperature and optimum excitation and emission wavelengths were found from recorded spectra. An appropriate amount of Tb^{3+}, 1 mL of 1×10^{-4} mol/L H_2PMBPP, 1 mL of 1.14×10^{-4} mol/L CPB, and 2 mL of hexamethylenetetramine (HALT) (5% w/w)-hydrochloric acid (pH=5.0) buffer were pipetted into a 25 mL calibrated tube, respectively. The mixture was diluted to 10 mL with de-ionized water. After 15 min, fluorescence determination was carried out at 549.5 nm with 272 nm exciting.

Terbium (III) is an unique ion which can form a stable fluorescent complex under the present experimental conditions. Other lanthanide ions do not show measurable fluorescence in this system.

Figure 1. Excitation spectra (a) and emission spectra(b)



1, 1′: system of Tb (III)-H_2PMBPP, 2, 2′: system of Tb (III)-H_2PMBPP-CPB [Tb]=1.0×10^{-6}mol/L, [CPB]= 1.14×10^{-5}mol/L, [H_2PMBPP] =1.0×10^{-5}mol/L, pH = 5.0 .

The hydrate a trivalent terbium ion fluoresced weakly at λ_{em}=549.5 nm, when irradiated with ultraviolet light λ_{ex}=272 nm, and when H_2PMBPP was introduced to the above system, the fluorescence intensity of the solution was enhanced. However, when CPB was added into the above system, the fluorescence intensity of the mixture solution was enhanced remarkably. Under optimum conditions, no appreciable emissions at the above emission wavelengths were observed for the free reagents.

The influence of the chemical variables on the system Tb (III)-H_2PMBPP-CPB was investigated separately in order to determine the optimal conditions for implementation of the proposed method. In this paper, three kinds of cationic surfactants, *i.e.*, N-cetylpyridium chloride, N-cetylpyridium bromide, cetyltrimethyl ammonium bromide; one kind of anionic surfactant, sodium dodecylbenzene sulfonate; and two kinds of non-ionic surfactants, *i.e.*, Triton X-100 and polyethylene glycoloctaphenyl ether were tested. However, when CPB was introduced in the system, the complex emits the strongest fluorescence, so CPB was selected in further experiments.

The effect of H_2PMBPP and CPB concentration on the fluorescence intensity were investigated, respectively. When the concentration of H_2PMBPP was controlled in the range from 9.5×10^{-6} to 1.1×10^{-5} mol/L, and the concentration of CPB was 1.14×10^{-5} mol/L, the system showed the strongest fluorescence intensity. In further experiments 1.14×10^{-5} mol/L CPB solution was employed and 1.0×10^{-5} mol/L was selected as optimum H_2PMBPP concentration.

In the presence of CPB and H_2PMBPP, the emission intensity remained constant in the pH range of 4.42～5.53. The working pH was thus adjusted to a value within that range.

The effect of time on the fluorescence intensity was investigated with 0.04767 μg/ml Tb (III) in HALT-HCl buffer solution (pH=5.0). The solution was allowed to stand under room temperature. The maximum fluorescence intensity can keep at least 7.5 h. The solution that was stood seven days caused a reduction of 50% in the fluorescence intensity.

Ions NH_4^+, K^+, Ac^-, PO_4^{3-}, SiO_3^{2-}, Br^-, F^-, Ca^{2+}, SO_4^{2-}, Na^+, Al^{3+} do not interfere with the determination of terbium. If an error of ± 5% in the fluorescence intensity was allowed in the determination of 0.1589 μg/mL Tb (III), the tolerance limits (tolerance fold) of various ions are: Mg^{2+}(200), Ba^{2+}(200), Zn^{2+}(150), Fe^{2+}(30), Ni^{2+}(160), Cu^{2+}(15), Fe^{3+}(5), La^{3+}(15), Ce^{3+}(55), Pr^{3+}(2), Nd^{3+}(12), Sm^{3+}(1/2), Eu^{3+}(1), Dy^{3+}(62), Ho^{3+}(40), Er^{3+}(5), Tm^{3+}(3), Yb^{3+} (15), Lu^{3+} (14), Gd^{3+} (3), Sc^{3+} (1/2).

The stoichiometry of the Tb (III)-H_2PMBPP-CPB system was determined under the established experimental conditions by Job's continuous variation method. The results indicated that the composition ratio of H_2PMBPP to Tb (III) is 2:1 and CPB to Tb (III) is 1:1.

The calibration graph for the determination of Tb (III) was constructed under the optimal conditions. Excellent linearity was obtained over the range 1.2×10^{-3} ~ 0.1589 μg/mL and 1.43×10^{-5} ~ 1.2×10^{-3} μg/mL of Tb^{3+} respectively. The detection limit was down to 3.178×10^{-6} μg/mL. Corresponding regression results were $F = 53.6267 + 169.2698\, C_{Tb^{3+}}$ (R = 0.99709, and SD = 0.016 for 10 measurements) and $F = 39.6144 + 1026.7751\, C_{Tb^{3+}}$ (R = 0.99764, and SD = 0.024 for 20 measurements) respectively.

The proposed method was used to the determination of trace Tb (III) in Baotou rare earth sample and synthetic sample[5]. The relative fluorescence intensities were measured and the results are shown in **Table 1.**

Table 1 The results of the determination of trace amounts of terbium in ore samples

Ore samples	Given value ng/ml	Found value ng/ml	Average value ng/ml	RSD (%)[a]
Fergusonite ($YNbO_4$)	6.35	6.55, 6.36, 6.41, 6.45, 6.28	6.41	1.56
Standard sample	12.00	12.05, 12.31, 12.48, 12.37, 12.28	12.30	1.30

[a]Relative standard deviation

Acknowledgments

The authors are grateful for financial supports from the National Natural Science Foundation of China and the Educational Commission of Gansu Province.

References

1. J. S. Du, *Hehuaxue Yu Fangshehuaxue*, **1985,** *7*, 182.
2. Y. D. Chen, X. F. Shi, J. J. Mao, H. F. Du, Y. Wang, L. Fu, *Hehuaxue Yu Fangshehuaxue*, **1992,** *14*, 213.
3. G. H. Jia, S. Y. Liu, T. F. Zhang, *Hehuaxue Yu Fangshehuaxue*, **1992,** *14*, 31.
4. J. S. Du, *Hehuaxue Yu Fangshehuaxue*, **1991,** *13*, 115.
5. "*Xitu Kuangwu Ceding Shouce*", Inst. Globe-Chemistry of the Academy of Sciences of China, **1977,** p318-359.
6. The amount of component ions per 100 mg of the synthetic sample, Fergusonite, are Ca (25.74), Mg (0.288), Mn (0.03), Pb (0.138), Fe (II) (0.114), Fe (III) (0.354), Al (1.176), U (2.376), Th (0.613), SiO^{2-}_3 (0.078), Ti (0.906), Nb (0.27), Ta (1.5), Eu (0.2), Gd (1.8), Tb (0.48), Dy (4.48), Ho (1.36), Er (2.76), Tm (0.52), Yb (2.96), Lu (0.744), Y (22.48).
7. The standard sample is produced by Rare Earth Institute of Baotou, Baotou. Its composition is as follows: Eu (0.49), Gd (4.4), Tb (3.14), Dy(11.1), Ho (3.3), Er (6.7), Tm (1.3), Yb (7.3), Lu (1.86) and Y (55.0).

Received 1 December 1999