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Estimation of Tb^{3+} by mellitic acid sensitized luminescence in methanol

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Mellitic acid sensitized luminescence of Tb^{3+} in methanol exhibits a strong emission which is about 500 times more intense than that observed in water. Under optimal conditions, the luminescence intensity exhibits an excellent linear relationship in the concentration range of 5×10^{-10}–5×10^{-8} *M* with a detection limit of 3×10^{-11} *M*. The interferences due to other lanthanides have been examined and found to be tolerated up to about 100-fold excess and hence estimation of Tb^{3+} in the presence of excess of lanthanides is possible. This method has been applied to the estimation of Tb^{3+} in simulated rare earth and tap water samples and the result is comparable to the result obtained from ICP-MS. Mechanism of enhanced luminescence is also proposed. This is the first report where mellitic acid sensitized luminescence is applied for the estimation of Tb^{3+}.

Keywords: Analytical chemistry, Luminescence, Rare earths, Lanthanides, Terbium, Mellitic acid

Terbium, an important member of rare earth family, has attracted significant interest in recent years. It is used in alloys, fluorescent phosphors, thermoluminescence dosimeter, etc.[1-7] There has been an increase interest of terbium in geochemistry, bioorganic and inorganic chemistry studies in recent times[8-12]. In addition, it has extensive applications in the research of proteins and detection of cancer cells by fluorescence imaging[13-18]. Due to its increased use in different fields and increased discharge toxic properties[19,20], determination of terbium has been the subject of current analytical research.

Instrumental methods, namely, ICP-MS[21,22] and ICP-AES[23-25] have been reported for the quantitative determination of trace levels of rare earths elements. These methods have drawbacks such as cost of the equipment and sometimes need for separation from major elements or pre-concentration, prior to determination of Tb^{3+}. A few reports on Tb^{3+} selective fluorescent sensors and membrane electrodes are available in the literature[26-30]. There are also some reports on Tb^{3+} assessment based on ligand sensitized luminescence (LSL)[31-36]. From the point of cost of analysis and simplicity, LSL is preferred over ICP based analysis.

Many aromatic carboxylic acids have been reported as suitable ligands for luminescence enhancement of lanthanides in aqueous medium[37-40]. However, these reports have rarely discussed about the application of the LSL for low level determination of lanthanides, particularly Tb^{3+}. Usually the luminescence of these aromatic carboxylic acid-lanthanide complexes is not sufficient enough for trace level detection of lanthanides. Generally, two methods are used for further improvement in the sensitivity of LSL. One of the methods is based on co-luminescence, where addition of certain lanthanides enhances the LSL further[13,31,41-43]. Another way of improving the sensitivity of LSL is by protecting the lanthanides from collision with water molecules using neutral ligands such as trioctyl phosphine oxide (TOPO), organic phosphates etc.[44-46]

Reduction of non-radiative decay channels due to collisions with water molecules can also be achieved by changing the medium from aqueous to non-aqueous. Recently, improvements in LSL of UO_2^{2+} and Eu^{3+} have been reported by changing the medium from aqueous to acetonitrile[47-49]. The solvent acetonitrile used in these studies provided a less aqueous environment around the metal complexes and hence there is reduction in non-radiative decay channels due to collisions with water molecules.

In the present study, we have examined the possibility of enhancing the mellitic acid (MA) sensitized luminescence of Tb^{3+} by changing the solvent from aqueous to non-aqueous. Mellitic acid has been reported to serve as a strong ligand for lanthanides in aqueous medium and about three orders of luminescence enhancement were reported for Tb^{3+} by this ligand[50]. However, this enhancement is not sufficient for its application in the determination of Tb^{3+} where low concentration needs to be estimated. In this regard, co-luminescence method can be applied, but since the interference from the other rare earths ions cause a serious problem, it is not suitable in many cases. Several non-aqueous solvents were tested to find out the enhancement in luminescence of Tb^{3+} and it was found that the degree of enhancement was different in different solvents with methanol showing a maximum enhancement. The enhancement observed in methanol is about two orders more compared to that in aqueous medium. Based on this, a method for the determination of Tb^{3+} has been developed. Presence of other rare earth ions in 100-fold excess concentration did not interfere in the luminescence intensity of Tb^{3+} and hence this method has been successfully applied for the estimation of Tb^{3+} ions in synthetic samples containing many rare earth ions. Also, the mechanism for the enhanced luminescence is proposed based on luminescence lifetime data. To the best of our knowledge this is the first report on application of MA sensitized luminescence of Tb^{3+}.

Materials and Methods

All luminescence spectra were recorded using an Edinburgh FLS920 spectrofluorimeter, with a 450 W xenon lamp as an excitation source. Solutions were taken in a 2 mm path length fused silica cell. The band pass for the excitation and emission monochromators was set at 3 nm each. A long-wavelength pass filter, (UV-39, Shimadzu) with a maximum and uniform transmittance (>85%) above 400 nm, was placed in front of the emission monochromator to reduce the scatter of the incident beam falling into the emission monochromator. Spectra were recorded at room temperature with a 90° collection geometry. Phosphorescence spectrum of gadolium-MA complex (in ethanol) was measured at liquid nitrogen temperature.

Lifetimes of Tb^{3+} and its complexes were recorded using a μs Xe-flash lamp, as an excitation source. Luminescence life times were determined by fitting the observed time resolved luminescence signals to an exponential decay function. A single exponential fit was found to be adequate for the decay processes observed in this study. The χ^2 values of all the fits ranged between 1.0 and 1.3. The lifetimes were extracted through a tail-fit, where the data points in the decay profile extending to long temporal regions were used in the fitting procedure. The error in the determination in lifetime is about 10%.

UV-vis absorption spectra were recorded using Avantes fiber optic spectrophotometer (AvaSpec-2048 with 300 lines per mm grating) with 10 mm path length cell.

Stock solution of terbium (10^{-1} *M*) was prepared by dissolving 0.0935 g of Tb_4O_7 (Indian Rare Earths, 99.9%) in concentrated $HClO_4$ and evaporated to dryness. The residue was then dissolved in a 5 mL flask by adding water to get the required concentration. From this stock, solutions of different concentration of Tb^{3+} were prepared for further use. It is to be noted that stock solution contains Tb^{3+} ions since in aqueous medium it is the most stable form. Stock solution of mellitic acid (10^{-1} *M*) (TCI, Japan, >98%) was prepared by dissolving the required amount of the reagent in water. All the solvents, dimethyl sulphoxide, acetonitrile, ethanol and methanol, used in this study were of AR grade. All the chemicals were used as purchased from the supplier. De-ionized water (18 MΩ) obtained with a Milli-Q (Millipore) system was used for the preparation of these solutions.

To record the spectrum, Tb^{3+}-MA complexes were prepared in water by mixing the required amount of MA and Tb^{3+} solution from the stocks and then adjusting the pH to the desired value. Then, 5 μL of this complex solution was mixed with 500 μL of solvent and the luminescence spectrum was recorded. However, to record the absorbance spectra, 20 μL of the complex solution was mixed with 2000 μL of the solvent. Therefore, in all the experiments (absorbance and luminescence) which were carried out in different solvents, 1% of water was present to begin with.

Results and Discussion

Herein, the term uncomplexed and complexed Tb^{3+} refers to Tb^{3+} specie in solvent/aqueous medium without and with MA respectively. Also the term pH implies the pH of aqueous solution of Tb^{3+}-MA prepared at a given pH from which 5/20 μL was taken and dissolved in the required amount of solvent.

Luminescence of Tb^{3+}-MA in different solvents

Figure 1 compares the excitation spectra of Tb^{3+}-MA complexes in different solvents such as methanol,

ethanol, dimethyl sulphoxide, acetonitrile and water. In all these experiments, the concentration of MA and pH were kept constant at 1.0×10^{-4} *M* and 8.5 respectively. The concentration of Tb^{3+} used in aqueous medium was 1.0×10^{-6} *M* whereas in all the other solvents it was 2.5×10^{-8} *M*. All the spectra were recorded by keeping the emission wavelength at 544 nm. It is clear from Fig. 1 that the excitation maximum is around 260 nm in all the cases. Figure 2 compares the emission spectra of Tb^{3+}-MA complexes in different medium by keeping the excitation wavelength at 260 nm. From Fig. 2 we can infer that the luminescence intensity of Tb^{3+} is more in organic solvents (curves 2-5) than in water (curve 1). The luminescence intensity of Tb^{3+} in Tb^{3+}-MA complex shows the following trend: Water < Acetonitrile < Ethanol < Dimethyl sulphoxide < Methanol. It has been reported in an earlier study that the luminescence intensity of Tb-N,N′,N″-tri (3-indolemethanal) triaminotriethylamine complex in different solvents was directly proportional to the permittivity values of the solvents[35]. The permittivity values of these organic solvents are 46.7 for dimethyl sulphoxide, 37.5 for acetonitrile, 32.6 for methanol and 24.3 for ethanol[35]. From Fig. 2 it is clear that there is no direct correlation of luminescence intensity of Tb^{3+}-MA complex with the permittivity values. Yang *et al.*[51] also did not observe any correlation of luminescence intensity with the permittivity values of solvents in the case of Eu^{3+} in its complex with a bis-Schiff base ligand. Another factor which is responsible for the changes in luminescence intensity of a given ion or its complex is the presence of –OH oscillators in the medium used. Even though deactivation pathways due to –OH oscillators are not present in the case of acetonitrile and dimethyl sulphoxide, less luminescence was noticed in these cases compared to that of methanol. The absorption spectra of Tb^{3+}-MA complex recorded in different solvents (Fig. 3) show that the absorbance of the complex at 260 nm (this is excitation maxima of the complex in all solvents) is highest in case of methanol (curve 5). In the case of ethanol medium, the absorbance intensity is almost the same as that in methanol medium (curve 4), but the emission intensity (Fig. 2, curve 3) in ethanol for this complex is nearly half of that in methanol (Fig. 2, curve 5). In the case of dimethyl sulphoxide, the absorbance (Fig. 3, curve 2) is the least, but the same is not true for emission. These observations clearly indicate that the luminescence intensity of an ion or its complex depends on a combination of factors such as absorbance, polarity, coordination ability and presence of deactivation pathways. As highest luminescence was observed for Tb^{3+}-MA complex in methanol medium, the same has been selected as the solvent for further studies.

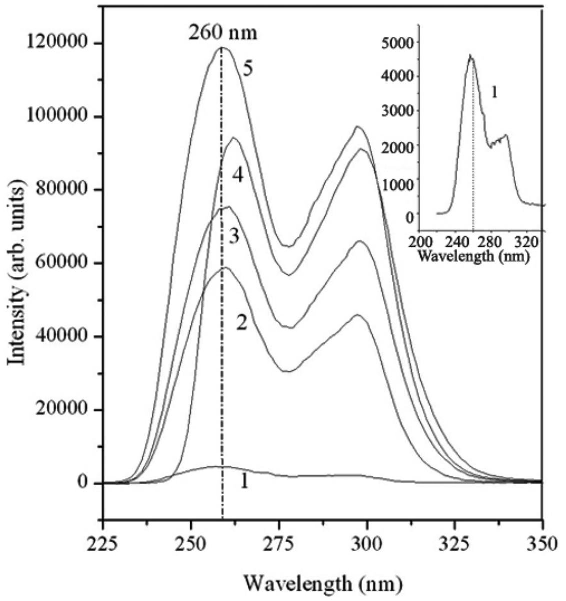

Fig. 1 — Excitation spectra of Tb^{3}-MA (1×10^{-4} *M*) in (1) water, (2) acetonitrile, (3) ethanol, (4) dimethyl sulphoxide, and, (5) methanol. [Spectra were recorded by monitoring the emission at 544 nm. Conc. of Tb^{3+} in water: 1×10^{-6} *M*; in other solvents: 2.5×10^{-8} *M*. For clarity the spectrum recorded in water is shown as inset also].

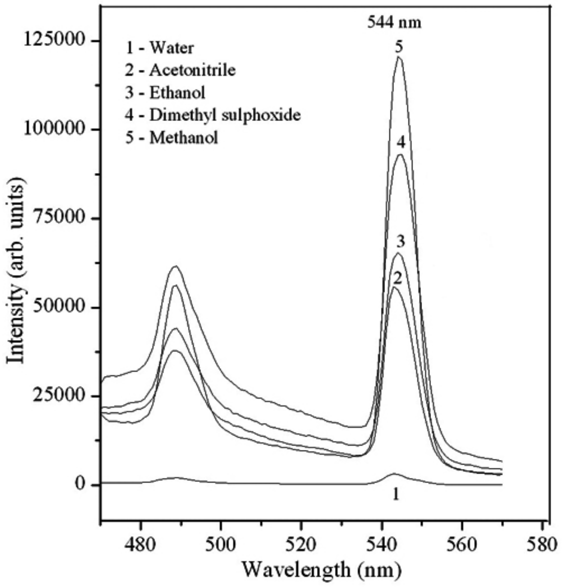

Fig. 2 — Emission spectra of Tb^{3}-MA (1×10^{-4} *M*) in (1) water, (2) acetonitrile, (3) ethanol, (4) dimethyl sulphoxide, and, (5) methanol. [Spectra were recorded by monitoring the excitation at 260 nm. Conc. of Tb^{3+} in water: 1×10^{-6} *M*; in other solvents: 2.5×10^{-8} *M*].

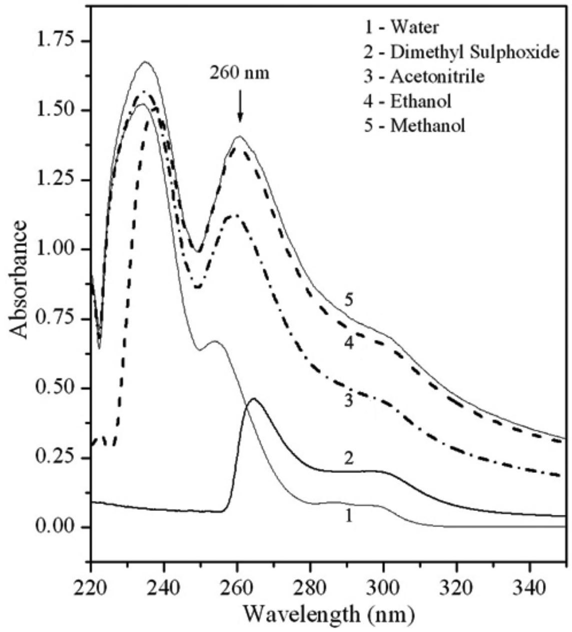

Fig. 3 — Absorption spectra of Tb^{3+} (2.5×10^{-8} *M*) – MA (1×10^{-4} *M*) in (1) water; (2) dimethyl sulphoxide, (3) acetonitrile, (4) ethanol, and, (5) methanol.

Luminescence of Tb^{3+}-MA in methanol

At the outset, the Tb^{3+} luminescence was measured as a function of the MA concentration and the pH of the solution. As ionization of MA depends on pH, it is important to measure the variation of luminescence with pH of the solution. Maximum luminescence intensity was obtained for a concentration of 1×10^{-4} *M* of MA over the pH 7.5-9.0. In the following experiments the concentration of MA and pH have been maintained at 1.0×10^{-4} *M* and 8.5 respectively.

The excitation spectrum of Tb^{3+} in methanol with the complexing ligand MA is shown in Fig. 1 (curve 5). The shape and the position of the excitation maximum are similar to the spectrum observed for Tb^{3+}-MA in water (Fig. 1, curve 1). Hence, the absorber is common in both cases and it is the ligand MA which sensitizes the Tb^{3+} luminescence.

Figure 4 compares the emission spectra of uncomplexed Tb^{3+} and Tb^{3+}-MA complex in water and methanol medium. The emission spectrum of Tb^{3+} in the Tb^{3+}-MA complex recorded in water and methanol respectively over the region 470-570 nm are shown in curve 2 and 4. The spectra shown here are blank subtracted and spectral corrected for instrument response. Both the spectra look similar to the emission spectrum of uncomplexed Tb^{3+} in water, shown in curve 1. For comparison the emission spectrum recorded for uncomplexed Tb^{3+} in methanol is also shown in curve 3. All spectra show characteristic sharp bands of Tb^{3+}. This suggests that the stock solution as prepared contains Tb^{3+} ions. The excitation wavelength used to record the uncomplexed Tb^{3+} was 351 nm, whereas for Tb^{3+}-MA complex it was 260 nm. Although the luminescence intensities shown here for complexed Tb^{3+} in methanol and water are comparable, the concentrations of Tb^{3+} used to record the spectra are different. The concentration of Tb^{3+} used to record the spectrum in methanol was 5×10^{-10} *M*, whereas it was 5×10^{-7} *M* in the case of water. The enhancement in luminescence is thus obvious and clearly indicates the role of methanol.

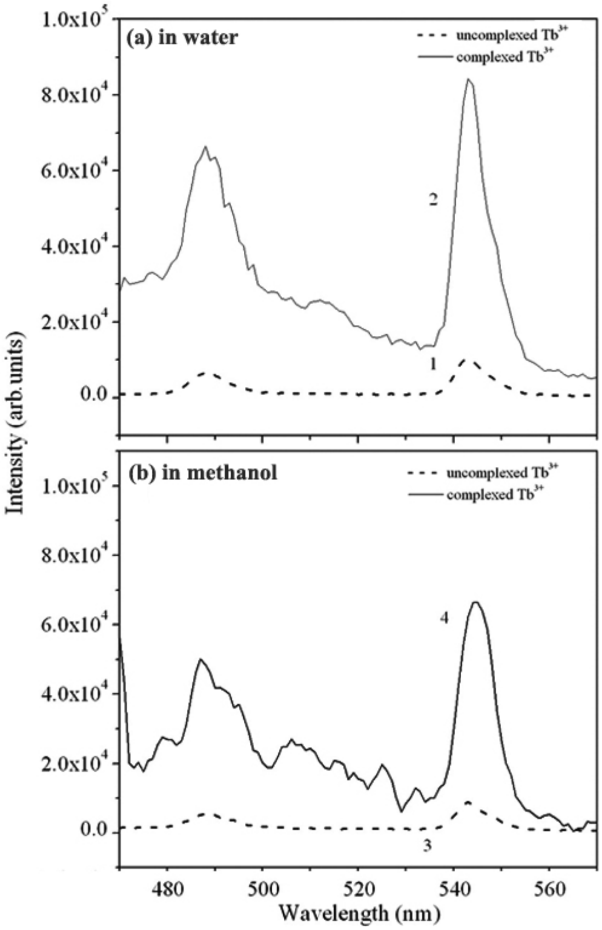

Fig. 4 — Emission spectra of Tb^{3+} in (a) water and (b) methanol. [1, Tb^{3+} (1×10^{-3} *M*); 2, Tb^{3+} (5×10^{-7} *M*)-MA; 3, Tb^{3+} (5×10^{-4} *M*); 4, Tb^{3+} (5×10^{-10} *M*)-MA. 1 and 3: λ_{ex} = 351 nm; 2 and 4: λ_{ex} = 260 nm].

Table 1 gives the luminescence enhancement factor and life time for Tb^{3+} in its acid complexes. Enhancement factor (EF) for Tb^{3+}-MA complex in a given medium was calculated as the ratio of Tb^{3+} concentration that gave the same luminescence intensity in uncomplexed Tb^{3+} and Tb^{3+}-MA complex. The intensity of 544 nm peak was used for calculating the EF. The value of EF in methanol is calculated to be 8.1×10^6, whereas it is only 1.6×10^4 in water, i.e., nearly 500 times enhancement in luminescence intensity is achieved by changing solvent from water to methanol.

The luminescence lifetimes of the Tb^{3+} emission in water and methanol are also presented in the Table 1. In water, the lifetime of Tb^{3+} in Tb^{3+}-MA complex is 520 µs and this is slightly more than the lifetime of 404 µs for uncomplexed Tb^{3+}, whereas in methanol a significant enhancement in lifetime was observed. The lifetime has increased from 526 µs for uncomplexed Tb^{3+} to 2850 µs for complexed Tb^{3+} in this medium. Increase in lifetime clearly indicates that the enhanced luminescence of Tb^{3+} in methanol is due to reduction in the non-radiative decay channels by displacing the water molecules from the coordination sphere. It is to be noted that the ~ 10^6 fold increase in intensity in methanol is not only due to increase in lifetime but also due to ligand sensitization. On the other hand in aqueous medium, about 10^4 times enhancement was mostly due to ligand sensitization as the lifetime increases by about 30% only.

Proposed mechanism of enhanced luminescence

It is known that the intramolecular energy transfer from ligand to lanthanides depends on the energy difference between the triplet level of ligand and the emissive energy level of lanthanides. The measured value of lowest triplet energy position of MA is 23440 cm^{-1}. As the emissive level of Tb^{3+} ($^5D_4$) is at 20500 cm^{-1}, efficient energy transfer can takes place from MA to Tb^{3+}.

In water MA forms 1:1 complex with lanthanides and it coordinates in a bidentate fashion[52]. In methanol, the lifetime of Tb^{3+} is very large in its MA complex (2850 µs) compared to uncomplexed Tb^{3+} (526 µs). This suggests that the stoichiometry of the complex could be different than 1:1. The lifetime (τ in ms) can be correlated with the number of water molecules (N_{H2O}) present in inner sphere of Tb^{3+} using the formula[53], $N_{H2O} = 4.0/\tau - 1.0$. From this formula, the number of water molecules coordinated to Tb^{3+} when it is uncomplexed is calculated to be 6.6. This indicates that nearly two water molecules are replaced by methanol molecules when the solvent is changed from water to methanol. In the same way, the number of water molecules coordinated to Tb^{3+} in its MA complex is calculated to be 0.4, indicating that nearly six water molecules are now replaced by MA upon complexation. Considering the bidentate nature of MA, the stoichiometry can be assumed to be 1:3. In an earlier study in acetonitrile medium, a similar observation was made when Eu^{3+} was complexed with benzoic acid (1:3) although in water medium it has been reported to form 1:1 or 1:2 complex[49]. Hence, the composition of the complex formed in our study is proposed as $Tb(MA)_3(methanol)_2$. Thus when methanol is used as a solvent, the non-radiative decay channels are reduced and also higher stoichiometric complexes are formed which we believe could be responsible for the enhanced luminescence in methanol.

Table 1 — Lifetime and enhancement factor (EF) of Tb^{3+} and its complex in different medium

Parameter	Tb^{3+} in		Tb^{3+}-MA in	
	Water	Methanol	Water	Methanol
Enhancement factor[a]	1	1	1.6×10^4	8.1×10^6
Lifetime (τ) in µs	404	526	520	2850

[a]Enhancement factor is the luminescence intensity relative to that of uncomplexed Tb^{3+} in the respective medium taken as 1.

Analytical parameters

For quantitative determination of Tb^{3+}, the calibration curve was obtained under the optimal experimental conditions. The linear range was found to be between 5×10^{-10} and 5×10^{-8} *M* of Tb^{3+} with a correlation co-efficient (R^2) of 0.9985 as shown in Fig. 5. The detection limit of Tb^{3+} in methanol (using

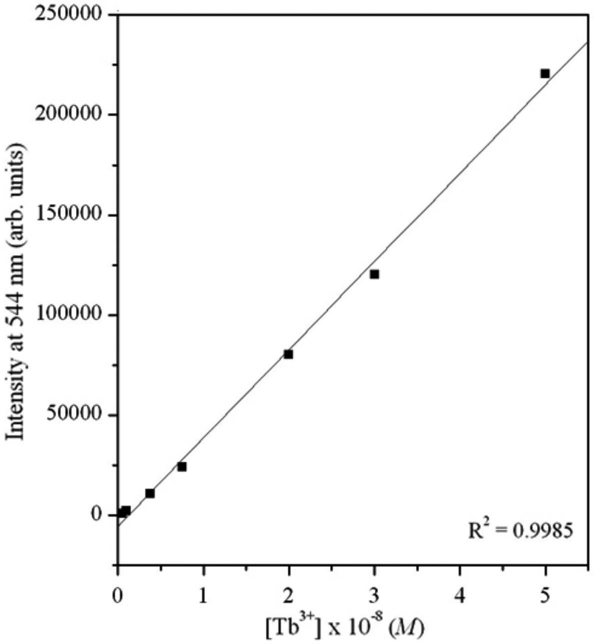

Fig. 5 — The calibration graph in the range of 5×10^{-10}-5×10^{-8} *M* for the determination of Tb^{3+}.

Table 2 — Comparison of limit of detection and dynamic range by different methods

System	Dynamic range	LOD	Ref.
Tb-La-ciprofloxacin-SDBS	8×10^{-10} to 5×10^{-6} *M*	1×10^{-11} *M*	31
Tb-trimesic acid-β-cyclodextrin/zirconate acid	0.508-521 ng/mL	-	32
Tb-EDTA-*o*-phenanthroline	0-15 ppm	30 ng/mL (1.9×10^{-7} *M*)	33
Tb-1,4,7,10-tetraazacyclododecane-1-[(N-oxido-pyridine-2-yl)methyl]-4,7,10-triacetic acid	-	0.9 μ*M* (9×10^{-7} *M*)	34
Tb-*N,N′,N″*-tri(3-indolemethanal)triamino-triethylamine-sodium acetate	5.7×10^{-11} to 6.3×10^{-6} *M*	5×10^{-11} *M*	35
Tb-nitrilotriacetate-tiron	3.3×10^{-9} to 3.3×10^{-7} *M*	1.6×10^{-10} *M*	36
Tb-mellitic acid	5×10^{-10} to 5×10^{-8} *M*	3×10^{-11} *M*	This work

Table 3 — The maximum permissible concentration of other ions for which change of intensities of Tb^{3+} is within 5% is given as multiples (M) of $[Tb^{3+}]$

Ions	M[a]	Ions	M[a]	Ions	M[a]
La^{3+}	400	Er^{3+}	100	Eu^{3+}	50
Nd^{3+}	112	Pr^{3+}	220	Ca^{2+}	100
Gd^{3+}	1600	Ce^{3+}	280	Mn^{2+}	70
Yb^{3+}	2000	Dy^{3+}	100	Li^{+}	1000
Lu^{3+}	2280	Sm^{3+}	40	SO_4^{2-}	1000
Tm^{3+}	124	Y^{3+}	200	CO_3^{2-}	100

[a]M: $[M^{3+}]$:$[Tb^{3}]$, where $[Tb^{3+}] = 2.5 \times 10^{-6}$ *M*.

Table 4 — Comparison of concentration of Tb^{3+} in synthetic samples

Sample	Conc. $[Tb^{3+}]$ (*M*)		
	As prepared	Present method	ICP-MS[a]
Oxide[b]	1.9×10^{-7}	$(1.8 \pm 0.24) \times 10^{-7}$	2.2×10^{-7}
Earth crust[c]	6.3×10^{-6}	$(5.3 \pm 0.46) \times 10^{-6}$	6.1×10^{-6}
Tap water	5.0×10^{-8}	$(4.6 \pm 0.40) \times 10^{-8}$	5.7×10^{-8}

[a]S.D. ~5%.

[b]Comp.: (Conc.×10^{-6} *M*) : Y : 2.7; La : 190; Ce : 350; Pr : 37; Nd : 120; Sm : 8.6; Eu : 1.5; Gd : 2.6; Dy : 0.56; Er : 0.16; Tm : 0.10; Yb : 0.10; Lu : 0.10; Tb : 0.19.

[c]Composition (Conc.×10^{-6} *M*) : Y : 350; La : 140; Ce : 310; Pr : 40; Nd : 170; Sm : 70; Eu : 7.2; Gd : 40; Dy : 27; Er : 14; Tm : 12; Yb : 15; Lu : 4; Tb : 6.3.

3σ criteria for blank) is 3×10^{-11} *M*. The relative standard deviation for five replicate analysis of the sample containing 5×10^{-10} *M* of Tb^{3+} is ~5%. Table 2 compares the analytical parameters of the present method with other spectrofluorimetric methods reported earlier[31-36]. The values of detection limits as reported[33-34, 36] are quite high (~10^{-10}-10^{-7} *M*). It can be seen from the table that the present method offers a comparable detection limit with other methods[31, 35].

The effect of some interfering ions including lanthanides on the estimation of Tb^{3+} by the proposed method was also studied. This study is necessary for the estimation of Tb^{3+} in rare earth ores. The concentration of Tb^{3+} in this study was chosen to be 2.5×10^{-6} *M*. The concentration of interfering lanthanides at which they caused a 5% change in intensity is shown in Table 3. While Sm^{3+} and Eu^{3+} affect the luminescence strongly, other lanthanides are tolerated at much higher levels. The effects of anions SO_4^{2-} and CO_3^{2-} are also found to be low. The tolerance limits of the interfering lanthanides in the present method are much better than the tolerance limits reported earlier[31-34,36] for the spectrofluorimetric determination of Tb^{3+}. These results indicate that the present method has great application potential for the detection of Tb^{3+} in rare earth oxide samples.

Application of the method

The proposed method was evaluated by estimating Tb^{3+} in synthetic mixtures prepared to mimic a) commercial oxide sample[54] and b) Earth's crust sample[31]. These samples were prepared by mixing suitable amounts of rare earths from standard stock solutions. The synthetic earth crust sample was diluted using distilled water appropriately before recording the spectra. In both cases, standard addition method was employed to arrive at the concentration of Tb^{3+}. The results obtained for these samples are given in Table 4. The method was also examined by adding known amounts of Tb^{3+} to tap water and the result is also listed in Table 4. The concentrations of Tb^{3+} were also quantified by the conventional ICP-MS method for validation. It can be seen from the results that the estimated concentrations of Tb^{3+} using both the methods are in agreement.

Conclusions

Mellitic acid sensitized luminescence of Tb^{3+} exhibits a 500-fold increase in luminescence intensity in methanol compared to aqueous medium. The measured life times of these complexes indicate that the enhancement of luminescent intensity is due to the reduction in the non-radiative decay channels in methanol medium. In methanol medium, the complex formed by mellitic acid with Tb^{3+} is $Tb(MA)_3(methanol)_2$. The effect of presence of other ions on the luminescence intensity Tb^{3+} was studied.

The estimation of trace levels of Tb^{3+} in synthetic mixtures of oxide ore and earth crust using ligand sensitized luminescence in methanol medium compared well with the values obtained from ICP-MS. This has demonstrated that estimation of Tb^{3+} in presence of large excess of ions is possible without any separation or pre-concentration procedures. This is a simple, rapid and sensitive method for the estimation of Tb^{3+}. Although mellitic acid sensitized luminescence in aqueous medium is a known phenomenon, but this has been explored for its analytical application for the first time in this report. Application of the present method is possible only if the solvent is changed from water to methanol.

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