Enhanced Luminescence of Lanthanides: Determination of Europium by Enhanced Luminescence

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Many advanced undergraduate analytical and physical chemistry laboratory courses employ experiments involving molecular luminescence. The popularity of luminescence is due primarily to the sensitivity and large linear dynamic range that can be obtained by using relatively modest equipment. As a rule, the experiment employs a highly fluorescent organic dye, typically a laser dye, and a serial dilution in an appropriate organic solvent to produce a calibration curve. Usually, efforts are directed toward quantitative measurements, since the qualitative aspects of luminescence measurements may be limited by the broad spectral bands of organic dye molecules. Some of the attractive features of luminescence spectroscopy are exemplified by this approach, but the dyes are frequently toxic or carcinogenic, the solvents toxic and flammable, and the need to perform trace analysis of laser dyes has limited practical application.

This paper presents an alternative approach for teaching the elements of luminescence spectroscopy based on the enhancement of lanthanide ion luminescence by complexation with a suitable coordinating ligand. This approach has several significant advantages over the more common experiment described above. First, all the chemicals used have limited toxicity, and no flammable solvents are required. Second, the proposed procedure ensures a large linear dynamic range and detection limits in the low- to sub-parts per billion range, even with very modest equipment. Third, the typically narrow luminescence bands exhibited by lanthanide ions make the inclusion of qualitative analysis in a mixture of lanthanides an easily added option. Finally, elements of coordination chemistry, mechanisms of intermolecular and intramolecular energy transfer, the spectral properties of lanthanide ions, and the role of solvent quenching may all be explored in a single simple experiment.

Complexation by certain organic ligands enhances the luminescence intensity of the tripositive lanthanide, Ln(III) ions. The enhancement of luminescence has been explained by a ligand to metal energy transfer mechanism (*1*). This mechanism for energy transfer was derived from a series of investigations by Kasha, Crosby, and their co-workers (*2*) and is illustrated in Figure 1. Generally, when an excited triplet state of the coordinating ligand overlaps a lanthanide excited electronic level, the lanthanide luminescence is effectively pumped by a large cross section molecular absorbance, rather than by its own weak absorbance. This process is much more efficient than direct absorption of light by the lanthanide owing to the poor absorptivities of the lanthanides (formally forbidden atomic absorbance for the intraconfiguration f → f transition) (*3*).

The energy level diagram adapted from Dieke (*4*) for selected lanthanides is shown in Figure 2. This diagram can
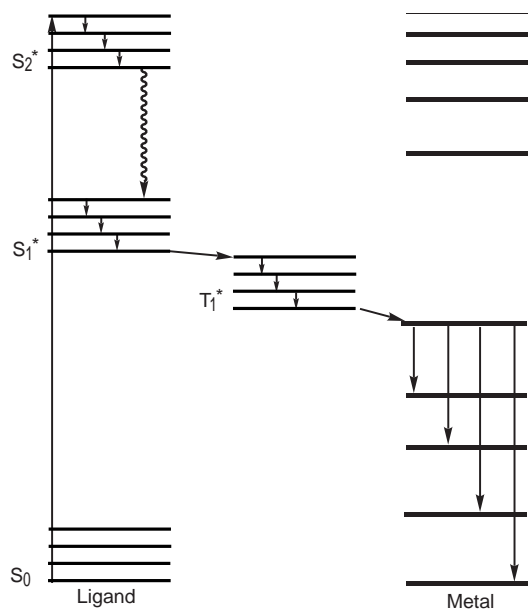

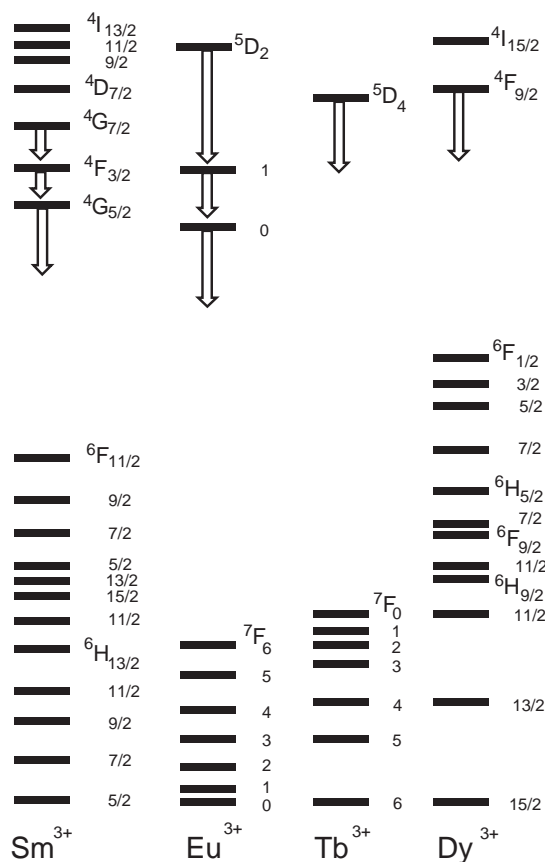Figure 1. Schematic diagram of the ligand-to-lanthanide energy-transfer mechanism.

Figure 2. Lanthanide(III) energy level diagram adapted from Dieke (*4*), showing the large energy gaps in low-lying levels. Levels that commonly luminesce are designated by downward arrows.

be used to illustrate the luminescent properties of the tripositive lanthanides. The elements shown in the diagram are those with the largest gaps in the energy level bands. These large band gaps allow the greatest luminescent intensities because they have longer decay lifetimes. Gadolinium, not shown here, also has an extremely large band gap; however, its excited levels are so high (300 nm, 730,000 cm^{-1}) that they are relatively inaccessible.

A large number of organic ligands have been used to enhance lanthanide luminescence intensity (2, 3). (The term luminescence is preferred here over fluorescence or phosphorescence because the intraconfigurational transitions may or may not involve a change in spin.) However, most of these ligands impose serious environmental hazards or difficulties in obtaining luminescence spectra by requiring special handling such as the use of flammable solvents or by being toxic. These considerations make experiments with these systems less suitable for student labs. Unlike these ligands, 2,6-pyridinedicarboxylic acid (dipicolinic acid, or DPA) is a relatively nontoxic, water-soluble alternative that is suitable for use in an upper-level undergraduate chemistry laboratory. An extensive article has recently been published in *Analytical Chemistry* detailing the characteristics of lanthanides complexed with DPA (5).

DPA is a tridentate ligand with an aromatic ring (**1**).

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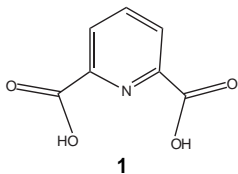
The carboxylic acid groups of the ligand help hold the nitrogen in the coordination sphere of the lanthanide ion, forming an efficient energy bridge. In the complex presented in this study, three DPA ligands coordinate the lanthanide ion, effectively saturating the coordination sphere. The relatively high coordination number of 9 is characteristic of lanthanides. For example, the aqua-ions of the lanthanides have coordination numbers ranging from 9 to 8 across the series, with the number gradually decreasing along the series owing to the lanthanide contraction (6). The higher coordination numbers result in less common coordination polyhedra such as the slightly distorted (site symmetry D_3 rather than D_{3h}) tricapped trigonal prismatic structure of this trischelated europium complex (7). For this complex, each of the ligands is positioned around the central ion in such a manner that the planar pyridine rings resemble the blades of a propeller (8, 9). The structure of the complex in solution has been verified by analyzing the luminescence spectra of frozen solutions (8).

Experimental Procedure

Instrumentation

Samples were placed in a quartz cuvette, though a plastic one may also be used. An Aminco-Keirs spectrophosphorimeter equipped with a xenon arc lamp and a 1P28A Hamamatsu photomultiplier tube was used to measure luminescence; however, any commercial fluorimeter or phosphorimeter can be used. Spectral scans were performed using an SLM Aminco 48000S spectrofluorimeter. If a pulsed excitation source such as a flash lamp, nitrogen laser, or pulsed dye laser and a gated or lock-in detection system are available, time-resolved measurements can be performed. This may result in improvements in linearity and limit of detection

(10). Linear regression was performed using Igor Pro software from Wavemetrics.

Preparation of Solutions

A 1.00×10^{-3} M Eu(III) stock solution should be prepared by dissolving high-purity (at least 99.9%) europium oxide with 1.0 M HNO_3 and diluting to the appropriate volume. A 0.1 M DPA stock solution should also be prepared using standard reagent-grade solid (available from Aldrich) and distilled water and heating with just enough 1.0 M NaOH to make it dissolve. Adjust the pH of this solution to 11 by the dropwise addition of 1.0 M NaOH. Both of these solutions can be prepared in advance.

Eu $(DPA)_3^{3-}$

Standard solutions of $Eu(NO_3)_3$ can be prepared by the students. These range from 10^{-5} to 10^{-11} M and decrease in semi-decade (10^{-5}, 5×10^{-6}, etc.) increments. $Eu(DPA)_3^{3-}$ standards with concentrations from 1.0×10^{-5} to 1.0×10^{-11} M can be prepared by combining 10.00 mL of each mid-decade $Eu(NO_3)_3$ solution (5×10^{-4}, … 5.0×10^{-10} M) with 10.00 mL of the 0.1 M DPA solution in 50-mL volumetric flasks and diluting to the mark. The mid-decade $Eu(DPA)_3^{3-}$ standards (5×10^{-5}, … 5.0×10^{-11} M) can be prepared by combining 25 mL of $Eu(NO_3)_3$ (1.0×10^{-4} to 1.0×10^{-10} M) with 25 mL of 0.1 M DPA solution. Then, if necessary, the solutions can be adjusted to the optimal pH 11 by the dropwise addition of 1.0 M NaOH. (This is normally not necessary, since the pH of the high ionic strength DPA solution was already established.) Once the pH is optimized, bring the solutions to the 50-mL mark by the addition of deionized water.

Luminescence Spectroscopy

Determination of Fluorimeter Settings

Set up each fluorescence spectrometer according to the operating instructions for that instrument. Fill the cuvette to be used with the most concentrated $Eu(DPA)_3^{3-}$ solution, and set the excitation wavelength to approximately 390 nm. Then, set the excitation and emission slits to the minimum width. With this done, the emission wavelength can slowly be scanned from 560 to 640 nm to determine the emission maximum. Using the emission wavelength that gave the maximum intensity, slowly scan the excitation wavelength from 350 to 420 nm to determine the excitation maximum. The excitation wavelength should be set to the value that corresponds to its maximum intensity. The maximum emission value obtained in this study was 619 nm, with the excitation set at 395 nm.
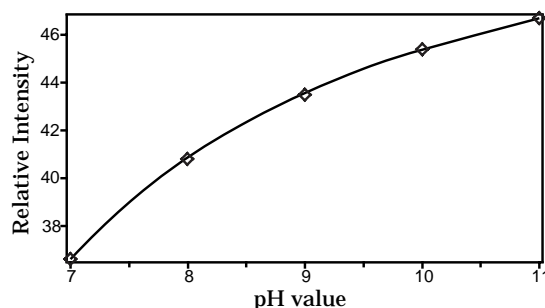

Figure 3. Graph showing the effect of pH on luminescence intensity of the europium chelate solutions. Excitation and emission wavelengths are 395 and 619 nm, respectively.

Table 1. Linear Calibration Curve Data

Conc. (ng/L)	Peak Area	
	$Eu(DPA)_3^{3-}$	$Eu(NO_3)_3^{3-}$
15.13	4.419	4.801
75.86	5.189	4.802
151.3	10.39	4.807
758.6	51.88	4.811
1,514	101.6	4.809
7,586	504.6	4.818
15,130	1109	4.833
75,860	6546	5.132
151,400	12,790	5.251
758,600	15,810	5.303
1,514,000	16,330	5.998

Table 2. Analytical Figures of Merit from the Linear Calibration Curves

Sample	LD	LDR	r	m
Eu^{3+}	6.9 ppm	7.6–760 ppm	.9977	0.049 area/ppm
$Eu(DPA)_3^{3-}$	48 ppt	0.152 ppm–76 ppt	.9998	0.085 area/ppt

Note: LD = limit of detection; LDR = linear dynamic range; r = correlation coefficient in LDR; m = slope of linear plot; ppm = mg/L; ppt = ng/L.

Table 3. Standard Addition Results

Sample	m	b	r	$Concn_x$
Tap water	0.461	2.75	.9985	90 ± 50 ppt
Pond water	1.25	17.9	.9982	22.2 ± 0.6 ppb

Note: m = slope (area/mL); b = y intercept; r = correlation coefficient in LDR; $concn_x$ = concentration of unknown; ppt = ng/L; ppb = μg/L.

pH Optimization

The optimal pH for the luminescence of this system can be found by taking one of the higher concentration $Eu(DPA)_3^{3-}$ samples ($\sim 10^{-5}$ M) and varying the pH from 7 to 11. Since DPA has a $pK_{a_1} = 2.16$ and $pK_{a_2} = 6.92$, pH values below 7 will cause the acid groups on the ligand to protonate, and the DPA will precipitate out of the solution (*11*). Elevation of pH beyond 11 may cause hydrolysis of the europium and precipitate the gelatinous hydroxide. The optimal pH was determined to be 11 (Fig. 3).

Calibration Curves

If calibrated cuvettes are not available, the students can mark one side of a cuvette so that the same side can always face the same direction. The cuvette should be filled with the most dilute solution (10^{-11} M Eu), and a series of replicate measurements (3 or more) can be made. This procedure is repeated for each of the concentrations, and a blank consisting of the DPA solution at the appropriate dilution. Next, the average intensity for each concentration is calculated (Table 1) and a calibration curve is constructed by plotting peak area versus concentration. Linear regression analysis yields the parameters listed in Table 2. Logarithmic values can also be plotted to clearly illustrate the large linear dynamic range (Fig. 4). Calibration curves for the europium nitrate solutions as well as the $Eu(DPA)_3^{3-}$ solutions are recommended, so the two systems can be compared. A limit of detection should be calculated for each system by
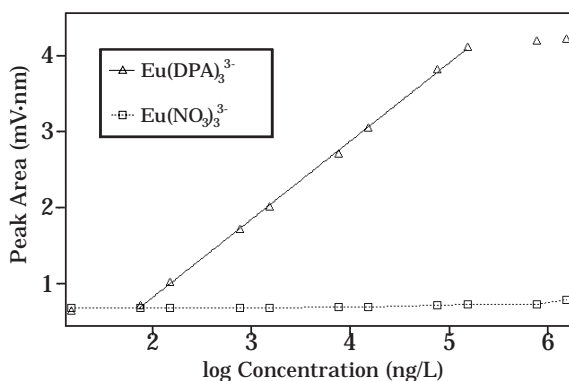
taking three times the standard deviation of the blank and dividing it by the slope (*10*).

Analysis of an Unknown

Trace amounts of rare earth elements such as europium can be found in many common water sources. Once the optimum system with the lowest LOD has been identified, the $Eu(DPA)_3^{3-}$ complex can be used to determine the europium concentration in an unknown such as tap water or water from a pond or stream. The narrow bandwidths of the lanthanides help assure that the luminescence is due to the europium and not other constituents in the matrix. Further verification of the presence of europium can be accomplished by scanning the emission wavelengths of the sample and identifying the characteristic europium bands (Fig. 5). Tap water at the University of Maryland Baltimore County was found to have a europium concentration of 90 ± 50 ppt. Pond water was analyzed and found to contain 22.2 ± 0.6 ppb europium.

To eliminate interferences, "real" samples should be analyzed by the method of standard addition (*10*). For these analyses 10.00 mL of sample can be used, along with 20.00 mL of the 0.1 M DPA solution added to a 50-mL volumetric flask. The samples can then be spiked with 0.0, 5.0, 10.0, and 15.0 mL of a 15.2 ppb standard for the pond water, or a 152 ppt standard for tap water. (The spike should approximately double or triple the expected unknown concentration.) Each of the samples can then be diluted to the 50.0-

Figure 4. Luminescence calibration curves for solutions of $Eu(NO_3)_3^{3-}$ and $Eu(DPA)_3^{3-}$. Excitation and emission wavelengths are 395 and 619 nm, respectively.
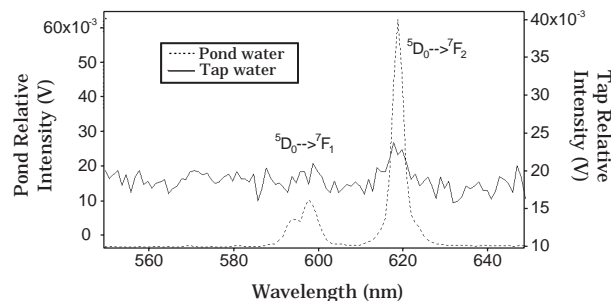

Figure 5. Emission spectra (raw data) of the tap water and pond water samples displaying the characteristic europium bands at 595 and 620 nm using a 395-nm excitation wavelength.
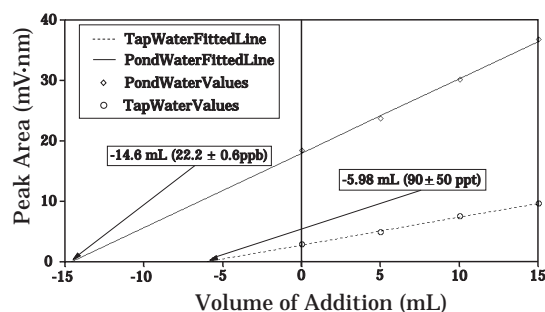
Figure 6. Standard addition plots for tap water and pond water samples. Pond water additions were made using a 15.2 ppb solution; tap water additions were made using a 152 ppt solution.
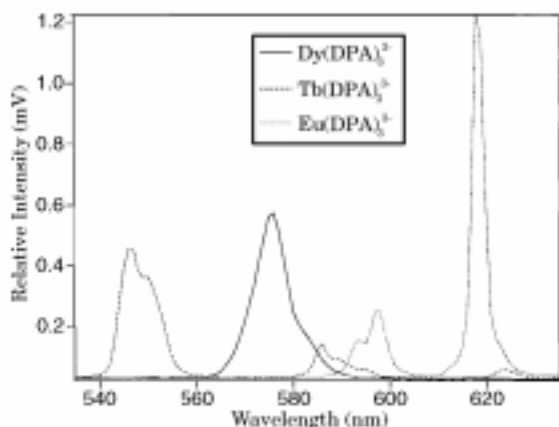

Figure 7. Luminescence spectra of a 1×10^{-5} M solution of (a) Eu(DPA)$_3^{3-}$,(b) Tb(DPA)$_3^{3-}$, and (c) Dy(DPA)$_3^{3-}$. Excitation wavelengths were 395, 320, and 368 nm, respectively.

mL mark with deionized water and analyzed as before. Finally, a standard addition plot can be constructed for each unknown (Fig. 6) and the europium concentration calculated (Table 2).

Additional Experiments

Terbium(III) solutions can be used as an alternative to europium; however, the fluorimeter settings will be different. The optimal excitation wavelength for terbium should be around 320 nm and the emission wavelength around 550 nm. Terbium can also be complexed by DPA to give enhanced luminescence. The characteristic luminescence color of terbium is green instead of the reddish-orange associated with europium.

Mixtures containing terbium, europium, and dysprosium with DPA can be unambiguously determined by first using a scanning instrument. Solutions of each lanthanide can be prepared in the same manner as the europium sample by mixing 10.00 mL of the corresponding 1.00×10^{-3} M nitrate solution with 10.00 mL of the 0.1 M DPA solution. (Again, the pH of these solutions should be basic.) The spectrum of each lanthanide solution should be scanned to determine the appropriate excitation and emission wavelengths for quantitative analysis. Mixtures of the lanthanides can then be analyzed using appropriate excitation/emission wavelength pairs. Individual lanthanides are easily identified by their characteristic emission spectra (Fig. 7).

Conclusions

This experiment was designed for use in an upper-level undergraduate instrumental or physical chemistry laboratory. It is safe and simple and can be performed using a variety of basic fluorescence instrumentation. The experiment introduces several important chemical and physical concepts. First, it explores the techniques of fluorescence spectroscopy. Second, it demonstrates that the lanthanides themselves exhibit weak luminescence, which can be enhanced by complexation with an appropriate ligand. The importance of pH for metal ion coordination is also explored. The experiment has ties to both physical and inorganic chemistry courses, by exploring molecular symmetry terms, point groups, and high coordination numbers. The effects of energy levels and orbital overlap are also demonstrated, and students learn how chemistry can enhance instrumental methods. Finally the analytical figures of merit exhibited by this method of analysis compare favorably with those from other current methods of analysis (1).

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