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Ultratrace Determination of Selected Lanthanides by Luminescence Enhancement

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The luminescence intensity of trivalent lanthanides, especially terbium(III) and europium(III), is shown to be enhanced by coordination with the ligand 2,6-pyridinedicarboxylic acid (DPA). Further enhancement can be obtained by forming a columinescent complex aggregate with ions such as gadolinium(III), terbium(III), lanthanum(III), or yttrium(III), where the Y(III) complex shows the greatest enhancement. A surfactant, sodium dodecyl sulfate (SDS), can be added to the solution to enhance the luminescence intensity of many lanthanide−ligand complexes by segregating the complex from quenchers. In this study, SDS has little effect on the limit of detection, but it does act to extend the linear dynamic range to include higher concentrations. The combination of columinescent complex with surfactant resulted in decreased luminescence intensity coupled with an increase in the background due to the light scattered by the surfactant micelles. A mechanism for the enhancement of the lanthanide luminescent intensity by energy transfer has been described by Xu et al. This study differs in that a lanthanide ion excitation band represents the most efficient excitation path and not a ligand excitation band. The complexes examined in this study have advantages over those used in prior studies since they do not require surfactants to achieve low limits of detection (100 parts per quadrillion, ppq, for Eu(DPA)$_3^{3-}$ and 60 ppq for Tb(DPA)$_3^{3-}$), and they exhibit longer linear dynamic ranges (from 4 to 6 decades) than other columinescent systems.

Some of the trivalent lanthanide ions exhibit excellent luminescence characteristics when the native luminescence is enhanced by coordination with suitable organic ligands. These properties include narrow bandwidths (typically a few nanometers), large Stokes shifts (hundreds of nanometers), relatively long luminescent lifetimes (up to milliseconds), and, in certain cases, anti-Stokes luminescence. These properties make trivalent lanthanide ions desirable as luminescent labels or probes for analytical determinations. A variety of methodologies have been developed to take advantage of these desirable luminescence characteristics. Recently, sensitized lanthanide luminescence has been applied to immunodiagnostic methods.[1] Radioactive labels and most organic dyes are hazardous, are limited in dynamic range, and pose storage difficulties due to their flammability or limited useful lifetime. Lanthanides are relatively innocuous due to poor absorption in the gastrointestinal tract and, even when injected, normally cannot penetrate living cells.[2,3]

The enhancement of luminescence intensity by complexation of the tripositive luminescent lanthanide, Ln(III), ions has been explained on the basis of a ligand-to-metal energy transfer mechanism.[4] This mechanism for energy transfer was derived from a systematic series of investigations by Kasha and Crosby and their coworkers.[5,6] It states that, when a coordinating ligand excited triplet state overlaps a lanthanide excited electronic level, the lanthanide luminescence is effectively pumped by the large cross-section molecular absorbance of the ligand rather than by the weak lanthanide absorbance. This process can be more efficient than direct absorption of light by the lanthanide, since the lanthanides exhibit low molar absorptivities.[7]

An abundance of articles on sensitized lanthanide luminescence have appeared recently. Most of the studies of ligand-sensitized lanthanide ion luminescence are based on older literature, describing complexes with β-diketone ligands.[8] These ligands usually produce eight-coordinate complexes, leaving an open coordination site susceptible to solvent coordination and luminescence quenching. More recent studies of the effects of countercation substitution of lanthanide complex anions have been accomplished using nine-coordinate complexes that make solvent coordination much more difficult. Many small organic ligands give higher coordination number complexes and enhance the lanthanide luminescent intensity.[9−13] Typically, these ligands impose limitations due to toxicity, flammability, and the need for complex matrices such as organic solvents or surfactants, or both.

Studies have also shown that lanthanide luminescence enhancement can be facilitated in complexes possessing an aromatic ring that has a nitrogen atom, such as 1,10-phenanthroline or bipyridine.[14−16] The nitrogen lone pair appears to form an efficient

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energy bridge to the lanthanide ion.[16,17] In a previous study of a variety of complexing agents, Miller and Senkfor determined 2,6-pyridinedicarboxylic acid (DPA) to be the most efficient ligand for sensitizing the luminescence of several lanthanide ions.[18] DPA is a tridentate ligand possessing an aromatic ring and has the advantage of being relatively nontoxic and nonflammable. In this complex, three ligands coordinate the lanthanide ion, effectively saturating the nine-member coordination sphere. The result is a complex that is soluble, less susceptible to solvent quenching, and intensely luminescent.[17,19] The relatively high coordination number, 9, is characteristic of the lanthanides.[20] This results in less common coordination polyhedra, such as the slightly distorted tricapped trigonal prismatic structure (site symmetry D_3 rather than D_{3h}) of this tris-chelated europium complex.[7] For this complex, ligands are arranged around the central ion in such a manner that the planar pyridine rings resemble the blades of a propeller.[17,19] The complex geometry has been verified for solutions by analyzing frozen samples.[19]

Several investigators have observed that adding an additional lanthanide ion to a solution with excess ligand increased the luminescence intensity due to a process known as columinescence.[1,8,11−13,21,22] An intermolecular ligand-to-ligand radiationless energy transfer is thought to occur between the donor complex and the luminescent compound. The concentration of the donor species is generally much greater than that of the acceptor complex; thus, each luminescent acceptor is surrounded by many donor chelates. Using a donor complex should enhance the luminescence by increasing the effective absorbance.[1] Studies of columinescence have had widely varying and often contradictory results. The most common columinescent ion additives were lanthanum, gadolinium, terbium, and yttrium. The ion that yields optimum enhancement and the optimal concentration of columinescent ion have varied from study to study.

A third means of luminescence enhancement for the ligand−lanthanide complex was the addition of a surfactant like sodium dodecyl sulfate (SDS) to the solution. Adding a surfactant results in the formation of micelles that create nonpolar regions in an aqueous solution.[16] This is useful since coordinated water has been shown to quench luminescence.[23,24] Intensity enhancements of 2 orders of magnitude or more may be encountered in luminescence analyses when micellar media are used.[25,26] Several of the lanthanide complexation systems previously studied relied heavily on micelles to enhance the luminescence. Micelles have also been used in conjunction with the technique of columinescence. However, the optimal micelle concentration and the optimal columinescent ion concentration, appear to vary greatly.

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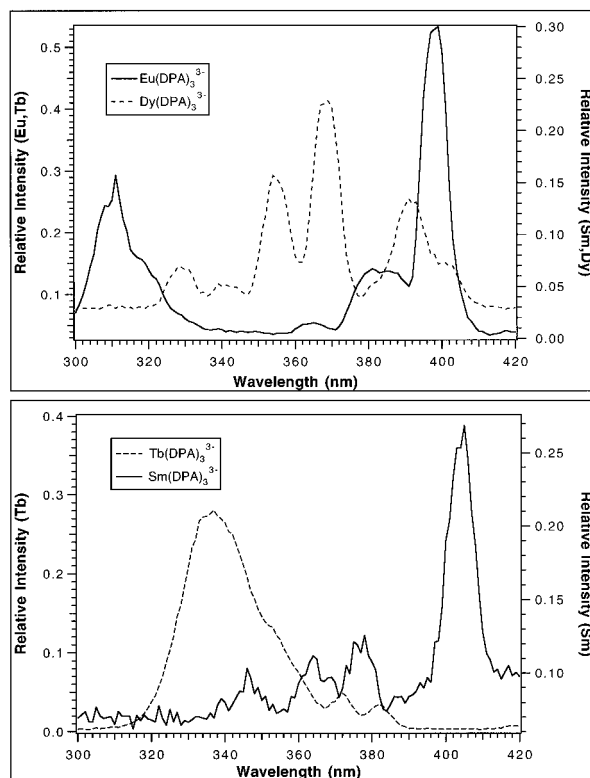(28) Yang, J.; Zhou, H.; Xuezhen, R.; Shi, R. *Analyst* **1990**, *115*, 1505−1510.

Figure 1. Excitation spectra of individual solutions of 1.0×10^{-3} M Eu(DPA)$_3$$^{3-}$, Dy(DPA)$_3$$^{3-}$, Tb(DPA)$_3$$^{3-}$, and Sm(DPA)$_3$$^{3-}$ at pH = 11 with emission wavelengths of 619, 576, 547, and 606 nm, respectively.

This may result simply from the ambiguity about the identity of the optimal columinescent ion.[26−28]

EXPERIMENTAL SECTION

Reagents. Unless otherwise indicated, materials were obtained from commercial suppliers and used without further purification. Analytical reagent grade chemicals were used along with deionized water to prepare solutions. The lanthanide oxides were obtained in purities of 99.9% or better, and yttrium was obtained as an atomic absorption standard. Stock solutions of 0.0100 M concentrations of the lanthanides were prepared by dissolving a known amount of oxide in 1.0 M nitric acid and diluting with water. Terbium was available only as a combination of the third and fourth oxidation states. A 1.00×10^{-2} M Tb(III) solution was prepared by dissolving 99.9% terbium(III,IV) oxide in concentrated nitric acid and heating in a hot water bath until the solution cleared. Working solutions were prepared by appropriate dilutions with 1.0% nitric acid in water.

Stock solutions of 0.100 M DPA were prepared by dissolving the appropriate amount in 1.00 M NaOH and diluting with water; this solution should have a final pH of 11.0. The 100 mM SDS solution was prepared by dissolving the appropriate amount of 99% SDS in water. A series of serial dilutions was made with deionized water.

Apparatus. All luminescence intensity measurements were made on an SLM 8000C spectrophosphorimeter equipped with SLM 48000S software (SLM Aminco Instruments, Urbana, IL). The instrument contains a Hamamatsu R-928 photomultiplier tube and an SA-309 xenon arc lamp. The luminescence intensities of the solutions were measured in 1.0 cm quartz cells. Luminescence measurements used excitation and emission wavelengths of 395
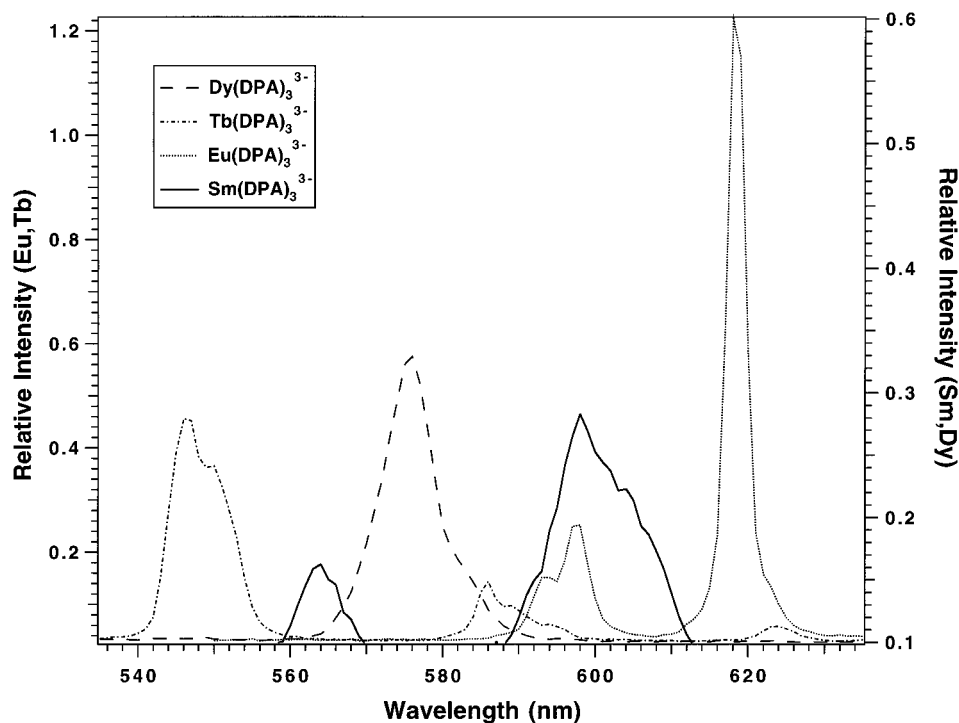
Figure 2. Emission spectra of individual solutions of 1.0×10^{-3} M Eu(DPA)$_3^{3-}$, Dy(DPA)$_3^{3-}$, Tb(DPA)$_3^{3-}$, and Sm(DPA)$_3^{3-}$ at pH = 11 with excitation at 395, 368, 338, and 405 nm, respectively.

and 619 nm for europium, 338 and 547 nm for terbium, 368 and 576 nm for dysprosium, and 405 and 606 nm for samarium, respectively. Excitation and emission spectra are shown in Figures 1 and 2, respectively. Europium concentrations in water samples were verified using a Hewlett Packard 4500 Series ICPMS Model G1820A (Hewlett Packard, Wilmington, DE). Graphs were plotted and graphical calculations performed using Igor Pro Software (WaveMetrics Inc., Lake Oswego, OR 97035).

Procedures. Eu(DPA)$_3^{3-}$, Sm(DPA)$_3^{3-}$, Dy(DPA)$_3^{3-}$, and Tb(DPA)$_3^{3-}$ standards, with concentrations from 1.00×10^{-5} to 1.00×10^{-14} M in semidecade increments, were prepared by combining appropriate volumes of each lanthanide nitrate solution with an equal volume of the 0.100 M DPA solution in 50 mL volumetric flasks. If necessary, the solutions were then adjusted to the optimal pH (11.0) by the dropwise addition of 1.0 M NaOH. (This was normally not necessary since the pH of the high ionic strength DPA solution was already established.) Once the pH was optimized, the solutions were diluted to the appropriate volume by addition of deionized water.

The pH for each system studied was optimized using a 1.00×10^{-5} M Eu(DPA)$_3^{3-}$ solution and varying the pH from 4 to 11 using water and either 1.00 M nitric acid or 1.00 M NaOH. The solution luminescence intensities were measured and compared, and the maximum intensity selected. Since the pK_{a_2} of DPA is 6.92, pH values below 6.0 were not used, since they would tend to cause the acid groups on the ligand to protonate and precipitate the DPA from the solution. Solutions of pH above 11 also were not used, since they precipitate the metal hydroxide from the solution.[29]

For the determination of the optimal columinescent ion concentration, standards ranging from 1.00×10^{-5} to 1.00×10^{-9} M Eu(DPA)$_3^{3-}$ were used. To determine the optimal columinescent ion and its optimal concentration, standard solutions of

Tb(III), Gd(III), La(III), and Y(III) were prepared from 5.00×10^{-3} to 1.00×10^{-11} M. Then, 10 mL of each solution was mixed with 20 mL of each of the europium complexes, and the luminescence was measured. The intensities were compared, and the maximum enhancing ion, along with the corresponding optimal concentration, was determined. Once this was established, calibration curves of Eu(DPA)$_3^{3-}$ and Tb(DPA)$_3^{3-}$ using the optimal concentration of columinescent ion as described above were made. A pH of 11.0 was maintained through all analyses.

The optimal SDS concentration was determined by preparing 10.0 mM increment standards from 10.0 to 100 mM SDS by serial dilution and combining 10 mL aliquots of SDS solution with 20 mL of the 1.00×10^{-5} M europium complex. The luminescence was measured, and the intensities were compared. Concentrations above 100 mM SDS were attempted but not used, since they tended to precipitate DPA or SDS from solution depending on the pH, resulting in intense light scattering.

The pH of the Eu(DPA)$_3^{3-}$ system with SDS was examined in the range of pH = 5−11 to determine the effect of pH on the micelle system. Two distinct behaviors were observed in this study. A more detailed appraisal of the two behaviors was obtained by constructing calibration curves at these two distinct pH values. Eu(DPA)$_3^{3-}$ solutions with SDS were prepared as described previously, and the pH was adjusted to both 11 ± 1 and 5 ± 1 using either 1.00 M nitric acid or 1.00 M NaOH to produce two calibration curves.

To examine the utility of the techniques on real samples, tap water and water from a pond on the University of Maryland Baltimore County campus were collected in acid-washed bottles on Jan 24, 1995. The samples were analyzed for europium using two versions (DPA only and DPA with Y columinescence) of this technique, employing the method of standard additions, and the results were compared to ICPMS analyses of the same samples. Emission scans of the water samples gave characteristic lanthanide

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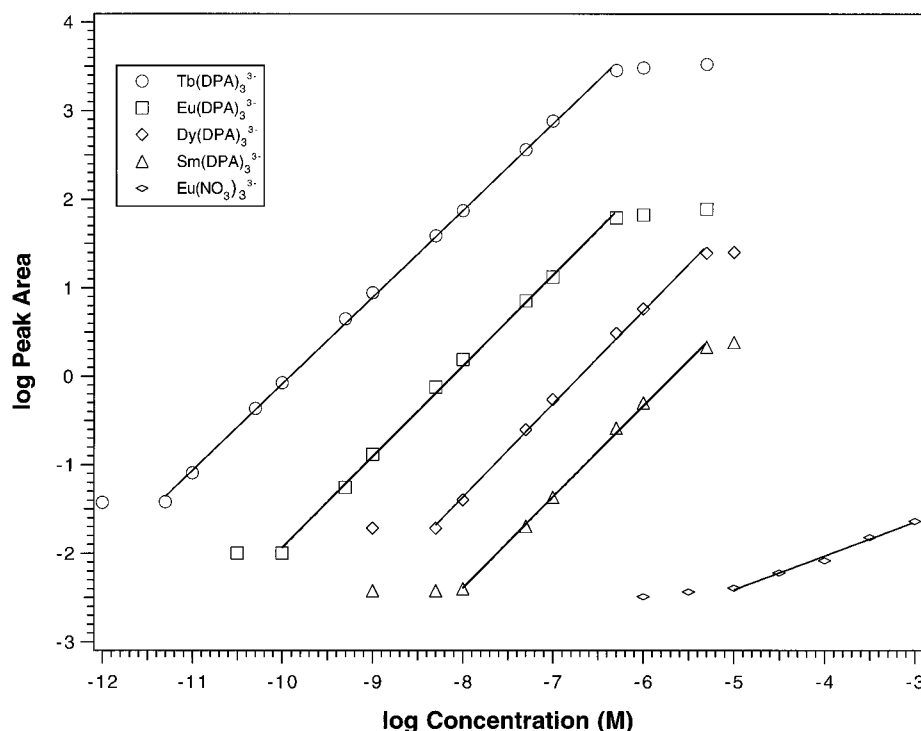
Figure 3. Calibration curves for sensitized luminescence for $Eu(DPA)_3^{3-}$, $Tb(DPA)_3^{3-}$, $Sm(DPA)_3^{3-}$, and $Dy(DPA)_3^{3-}$ at pH = 11, with unsensitized $Eu(NO_3)_3^{3-}$ (pH = 3) for comparison.

spectra. For the ICPMS analyses, the instrument was calibrated with 100, 125, and 150 ppt standards for the tap water samples and with 10, 20, and 30 ppb standards for the pond water samples. All standards were made with 1.0% nitric acid.

RESULTS AND DISCUSSION

Sensitized Luminescence. Calibration curves of $Eu(DPA)_3^{3-}$ and $Eu(NO_3)_3^{3-}$ as well as those for terbium, dysprosium, and samarium showed that, when DPA was added to a rare earth nitrate solution in a ligand−lanthanide ratio of 3:1 or greater, a significant enhancement of the rare earth's luminescence was observed (Figure 3). The nitrate solutions for samarium and dysprosium showed no detectable luminescence below 1.00×10^{-4} M, but, when complexed with DPA, they could be detected in the nanomolar range. The luminescence intensity of the terbium and europium complexes is also increased by several orders of magnitude over the corresponding nitrates. The rare earth−DPA system was optimized for pH from 7 to 11, where optimal pH was determined to be 11.

All limits of detection (LODs), were calculated using 3 times the standard deviation of the blank divided by the slope of the calibration curve.[30] The LODs for europium nitrate and $Eu(DPA)_3^{3-}$ are 22 ppb and 14 ppt, respectively. Terbium, samarium, and dysprosium showed similar improvements when complexed with the ligand. LODs for these lanthanides and analytical figures of merit are shown in Table 1. Linear dynamic ranges also increased when the lanthanides were complexed with the ligand. The linear dynamic range for the $Eu(DPA)_3^{3-}$ complex was 0.0015−75.98 ppb, as compared to the range of 150−151 900 ppb for the nitrate solution. These increases are relatively similar to the linear ranges of the other lanthanides, as provided in Table 1. The linear

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Table 1. Analytical Figures of Merit for Sensitized Luminescence

system	LOD (ppt)	LDR (ppb)	corr coeff.	slope
$Eu(NO_3)_3^{3-}$	20×10^4	$150-1.519 \times 10^5$	0.9997	3.17×10^{-7}
$Eu(DPA)_3^{3-}$	14	$1.5 \times 10^{-2}-75.98$	0.9996	8.16×10^{-3}
$Tb(NO_3)_3^{3-}$	20×10^4	$760-151.9 \times 10^3$	0.9993	5.67×10^{-8}
$Tb(DPA)_3^{3-}$	2.4	$1.5 \times 10^{-3}-75.98$	0.9985	1.19×10^{-2}
$Sm(DPA)_3^{3-}$	140	$1.5-75.98$	0.9998	8.31×10^{-6}
$Dy(DPA)_3^{3-}$	640	$7.6 \times 10^{-1}-75.98$	0.9993	8.08×10^{-5}

Table 2. Yttrium Columinescence As a Function of Europium Concentration[a]

Eu concn (M)	Y concn (M)					
	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}
10^{-5}	59	71	100	72	56	53
10^{-6}	30	40	63	38	28	19
10^{-7}	22	33	50	30	22	15
10^{-8}	9.2	25	37	24	15	7.7
10^{-9}	6.1	9.2	25	13	8.1	4.4
10^{-10}	2.8	4.9	12	6.6	3.0	1.1

[a] Values normalized to a maximum of 100.

dynamic range for this study is defined as the region of the curve where a line plotted through the data gives a correlation coefficient of 0.9985 or greater.

It was noted that there were several linear regions of the calibration curve when peak heights were plotted with concentration, and that these linear regions correspond to changes in the peak widths (Figure 4). These changes in peak height are believed to be a result of luminescent complex aggregation, consistent with the mechanism of columinescence.[1] Aggregation limits molecular motion, and the corresponding spectral peak
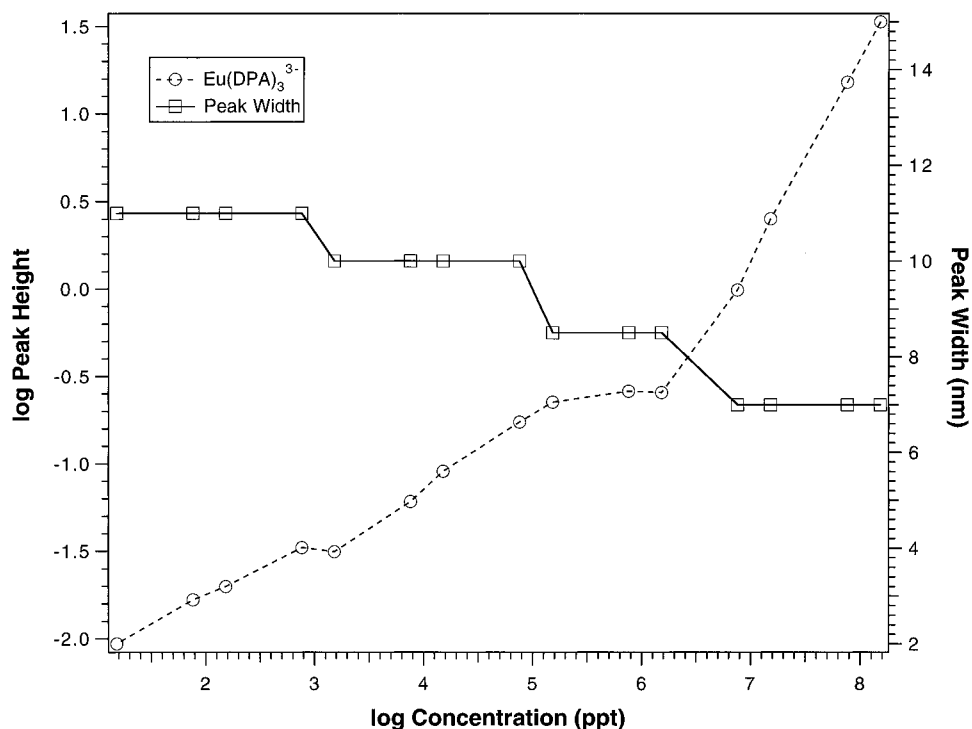
Figure 4. Peak width and peak height versus concentration for the $Eu(DPA)_3^{3-}$ system at pH = 11.
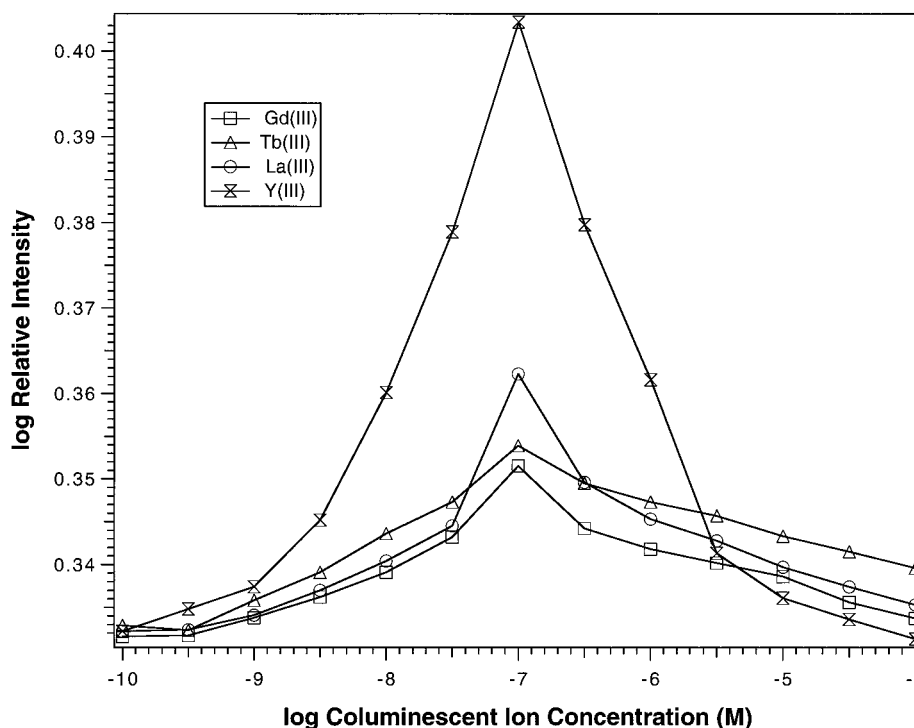

Figure 5. Optimization of columinescence concentration for various columinescent ions with 1.0×10^{-5} M $Eu(DPA)_3^{3-}$ and pH = 11.

width decreases. There appear to be four stages in the aggregation process, corresponding to the four linear regions of the curve. When peak area is substituted for peak height, longer linear ranges are observed (Figure 3).

Columinescence. The addition of a columinescent ion complex has been shown to enhance the luminescence of lanthanide ions. La(III), Y(III), Tb(III), and Gd(III) were chosen as columinescent ions for the determinations of $Eu(DPA)_3^{3-}$ and $Tb(DPA)_3^{3-}$. The optimal concentration of columinescent ion was found to be 1.00×10^{-7} M for all the columinescence-enhancing ions analyzed (Figure 5) using a 1.00×10^{-5} M Eu(III) matrix.

All of the columinescent ions showed some enhancement over the $Eu(DPA)_3^{3-}$ system at this optimal concentration. The optimization experiment was repeated with europium concentrations from 1.00×10^{-5} to 1.00×10^{-9} M to verify that the optimal concentration did not change with europium concentration. Table 2 shows the results of the entire study for yttrium. The order of enhancement was found to be yttrium, lanthanum, gadolinium, and terbium, in order of decreasing effect.

Columinescence is attributed to the formation of an ion complex that allows for greater absorbance and energy transfer to a luminescent ion sink. Lanthanum and yttrium ions should

Table 3. Figures of Merit for the Columinescence Analyses

system	LOD (ppt)	LDR (ppb)	corr coeff.	slope
$Eu(DPA)_3$	14	$15 \times 10^{-3} - 75.98$	0.9996	8.15×10^{-3}
$Eu(DPA)_3$ with Y	0.110	$1.5 \times 10^{-4} - 1.519 \times 10^3$	0.9997	5.55×10^{-2}
$Tb(DPA)_3$	2.4	$1.5 \times 10^{-3} - 75.98$	0.9985	1.19×10^{-2}
$Tb(DPA)_3$ with Y	0.056	$1.5 \times 10^{-4} - 1.512 \times 10^3$	0.9995	0.988
$Sm(DPA)_3$	140	$1.5 - 75.98$	0.9998	8.31×10^{-6}
$Sm(DPA)_3$ with Y	120	$7.6 \times 10^{-2} - 75.98$	0.9998	1.28×10^{-4}
$Dy(DPA)_3$	640	$0.76 - 75.98$	0.9993	8.08×10^{-5}
$Dy(DPA)_3$ with Y	53	$0.15 - 75.98$	0.9994	2.05×10^{-4}

Table 4. Analytical Figures of Merit for the Micelle Analyses

system	LOD (ppt)	LDR (ppb)	corr coeff.	slope
$Eu(DPA)^{3-}$	14	$1.5 \times 10^{-2} - 75.98$	0.9996	8.16×10^{-3}
$Eu(DPA)^{3-}$ with SDS	1.1	$1.5 \times 10^{-3} - 75.98$	0.9988	2.50×10^{-3}
$Eu(DPA)^{3-}$ with SDS & Y	22	$1.5 \times 10^{-2} - 1.519 \times 102$	0.9999	6.32×10^{-2}
$Tb(DPA)^{3-}$	2.4	$1.5 \times 10^{-3} - 75.98$	0.9985	1.19×10^{-2}
$Tb(DPA)^{3-}$ with SDS	1.8	$1.5 \times 10^{-3} - 1.519 \times 104$	0.9994	7.50×10^{-1}
$Tb(DPA)^{3-}$ with SDS and Y	23	$7.6 \times 10^{-3} - 1.519 \times 102$	0.9991	2.58×10^{-1}

perform similarly if the transfer of energy is facilitated through the coordinating ligands, since neither of these ions has any occupied f orbitals to produce an energy sink. The enhanced performance of Y(III) is believed to be due to a higher purity. The similarities of the lanthanide ions results in difficulties as Y(III) is likely to have lanthanide impurities that could act as additional energy sinks. This theory is supported by a study showing that, when lanthanum is obtained in a purity of 99.999% or better, its enhancement can equal that of yttrium.[1]

The effect of columinescence is observed as a vertical shift in the calibration curve. This results in an increase in the linear dynamic range into regions of lower concentration and improves the LOD by $\sim 1-2$ decades for all the lanthanide−DPA systems. The LOD for $Eu(DPA)_3^{3-}$ system decreases from 14 ppt to 100 ppq for the $Eu(DPA)_3^{3-}$ system with yttrium. The terbium LOD from 1.5 ppt to 56 ppq with yttrium. Linear dynamic ranges for these systems were also lengthened correspondingly. Lower LODs and longer linear ranges were also noted for samarium and dysprosium when yttrium was added (Table 3).

Surfactant. Adding a surfactant had a small effect on the luminescence intensities of the $Ln(DPA)_3^{3-}$ systems. Aliquots of SDS ranging in concentration from 10 to 100 mM were added to the $Eu(DPA)_3^{3-}$ solutions. A maximum luminescence intensity was observed with an SDS concentration of 50 mM at pH = 11. Concentrations of SDS above 100 mM were attempted, but the increased light scatter caused by the larger SDS concentrations overshadowed any enhancement. Higher concentrations of SDS often caused precipitation. $Eu(DPA)_3^{3-}$ with SDS calibration curves were prepared and LODs calculated (Table 4). The calibration curve produced when the pH was adjusted to ~ 5 did not differ appreciably from the curve without SDS.

The use of a surfactant does not substantially improve the LODs (from 14 to 1 ppt for europium) in this study as compared to other systems that have reported as large as a 1000-fold increase in luminescence when surfactants were used.[1] A time-resolved luminescence study performed on a series of Eu(III) complexes by Horrocks et al. shows a correlation between the number of water molecules coordinated to the Eu(III) and the luminescence lifetimes exhibited by the complexes.[23] This study gave the complex of Eu(III) with dipicolinic acid as an example of a complex

that had no coordinated water. Thus, since the complex already excludes water, the need for surfactants is almost eliminated. Surfactant effects were also investigated for the $Tb(DPA)_3^{3-}$ system, with similar results (Table 4).

Columinescence with SDS. Combining the effects of columinescence with the use of surfactants has been shown to have enhancing effects for some systems [9,11,12] and inhibitory effects on others.[24] Here, columinescence coupled with surfactants had the effect of decreasing the overall luminescence intensity, along with imposing a larger background and decreasing the signal-to-noise ratio. The solutions were prone to precipitation, and the detection limits were higher (Table 4). However, the linear dynamic range is increased over that of the sensitized complex.

The poor results obtained by the combination of these techniques may be attributed to several factors. First, the large amounts of dissolved solids involved in the combination of these techniques causes an increased background due to scattered light. Since the coordination sphere of the lanthanide ion is saturated by the ligand, the ability of water to quench the luminescence is small. Finally, SDS could inhibit the formation of columinescent aggregates. This combination of factors makes this technique ineffectual.

Water Analysis. An illustration of the applicability of the techniques presented in this paper was the analysis of environmental water samples. The samples were analyzed by the method of standard addition using both the technique of sensitized luminescence and Y(III) complex columinescence at pH = 11. Using the sensitized luminescence technique, tap water was found to have 90 ± 50 ppt and the pond water 22.2 ± 0.6 ppb europium. Using the columinescence technique, tap water was found to have 109 ± 9 ppt and the pond water 24.3 ± 0.2 ppb europium. ICPMS analyses were also performed on the samples for verification of technique validity. This was necessary since we were unable to find a suitable standard reference material and only ICPMS could give comparable LODs. Thus, tap water was determined to have 113 ± 7 ppt and the pond sample 24 ± 1 ppb europium. The results of the luminescence analyses fall within the standard error of the ICPMS reference method.

Energy Transfer Mechanism. The accepted mechanism for energy transfer is not supported in this study. In other studies,

optimal luminescence intensity occurred when the ligand band was excited directly. In this study, however, it was found that optimal luminescence intensity occurred not when the ligand band at 335 nm was excited, but rather when a specific lanthanide absorbance was excited directly. Absorption spectra of $Eu(NO_3)_3^{3-}$ and $Eu(DPA)_3^{3-}$ show that the coordination complex has a slightly larger absorptivity. This increase does not seem to be large enough to explain the large degree of sensitization afforded by the ligand. The underlying reason for this luminescence enhancement is being pursued.

CONCLUSIONS

Other techniques have been developed that enhance the luminescence intensity of the certain lanthanides with comparable detection limits. The technique presented here has advantages over other techniques in that it used relatively nontoxic and nonflammable components. It does not require the addition of surfactants or various synergistic reagents to achieve low detection limits and exhibits a larger linear dynamic range. This is accomplished without requiring time-resolved measurements, but it is likely that this technique could be enhanced with time resolution to give lower limits of detection and a longer linear range. One application for this technique would be as a nontoxic alternative for radioactive labels in various assays.[1,31−33] The large complexation constant for DPA with lanthanides (log $K_3 \approx 21$)[29] would facilitate their removal from labeled molecules.

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