Studies on Derivative Fluorimetry. II. Simultaneous Determination of Traces of Samarium, Europium and Terbium through their Ternary Complexes with 2-Thenoyltrifluoroacetone and Diphenylguanidine in the Presence of Triton X-100*

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Fluorimetric analysis is a highly sensitive method for the determination of rare earths and has received much attention [1–3]. In a recent paper [4], the derivative fluorescent properties of ternary complexes formed by some rare earths with 2-thenoyltrifluoroacetone (TTA) and diphenylguanidine (DPG) were investigated, and can be utilized for the determination of samarium, europium and terbium. In the present report a surfactant, Triton X-100, is added to the above system. The results show that in the quaternary system of Ln^{3+}–TTA–DPG–Triton X-100 a stable and strong fluorescence of these complexes was observed. Based on this characteristic of quaternary systems a very sensitive method is discussed for simultaneous determination of Sm, Eu and Tb.

Experimental

Standard solutions of Sm^{3+}, Eu^{3+} or Tb^{3+} were prepared by dissolving their corresponding oxides (99.99%) in $HClO_4$ and evaporating the solution to a syrup and diluting with ethanol to a constant volume. TTA and DPG solutions were obtained by dissolving these reagents in ethanol. Triton X-100 was used as 2.5 or 5.0% aqueous solutions. Ammonium acetate buffer solution (1 M) was used, pH = 6.90. The above reagents were of analytical grade.

All fluorescence spectra were obtained with a Hitachi MPF-4 spectrofluorimeter equipped with a xenon arc-lamp. The pH values of the solutions were measured with a pHs-2 meter. The experimental details may be found in ref. 4.

Results and Discussion

In the quaternary system of Ln^{3+}–TTA–DPG–Triton X-100, as we know, only the three ions of

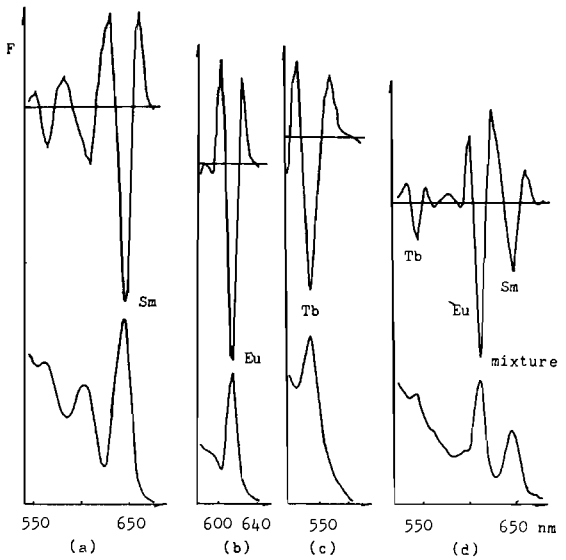

Fig. 1. Fluorescence spectra (lower curve) of the Ln^{3+}–TTA–DPG–Triton X-100 systems and their second-derivative spectra (upper curve). Conditions: 1.6×10^{-4} M TTA, 1×10^{-3} M DPG, 0.125% Triton X-100, 0.05 M NH_4Ac, pH = 6.90, Ex = 368 nm: (a) 2×10^{-7} M Sm; (b) 3×10^{-9} M Eu; (c) 5×10^{-6} M Tb; (d) 8×10^{-8} M Sm + 1.9×10^{-9} M Eu + 1.7×10^{-6} M Tb.

Sm^{3+}, Eu^{3+} and Tb^{3+} exhibit fluorescence properties. Figure 1(a, b, c) shows their fluorescence and second-derivative spectra separately. Figure 1d is a spectrum of a mixture of them. Because of a strong background, it is difficult to determine Sm^{3+}, Eu^{3+} and Tb^{3+} in the mixture by direct fluorimetry. If derivative fluorimetry is used, the interference from the background can be eliminated and very good sensitivity can be obtained.

The influence of pH and the amounts of various reagents used on the fluorescence intensity in this system were studied: in the pH range 6.6–7.1, the highest fluorescence intensity was observed; at pH > 9.5, the intensity became very weak because of the decomposition of TTA. The most suitable amounts of reagents were: 0.004 M TTA (0.4 ml), 0.02 M DPG (0.5 ml), 2.5% Triton X-100 (0.5 ml) and 1.0 M NH_4Ac (0.5 ml). The final volume was 10 ml.

Figure 2 shows the effect of the Triton X-100 concentration. As may be observed, with an increase in Triton X-100 concentration the surface tension becomes lower and lower. When the Triton X-100 concentration is as high as 1.9×10^{-3} M, (in general, this point was called the critical micellar concentration, abbreviated to CMC), the surface tension appears to no longer change. Moreover, the fluorescent intensity of the complex becomes a maximum, too, and maintains a contant value over a larger range of surfactant concentration.

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TABLE I. The Tolerance Limits of the Other Rare Earth Ions

Sample	Tolerance limit (μg)														
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Sm	20	1.6	0.5	0.5		0.1	16	20	8	0.5	1	0.5	4	2	1
Eu	20	1.6	0.5	0.5	0.8		20	20	8	0.5	1	0.5	4	2	1
Tb	8	1.6	0.5	0.5	0.5	0.1	20		8	0.5	1	0.5	4	2	1

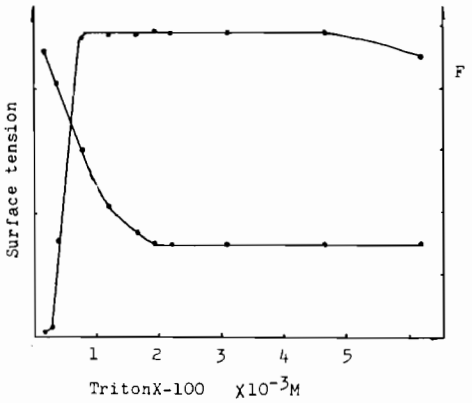

Fig. 2. Variations of fluorescence intensity (upper curve) and surface tension (lower curve) with increasing concentration of Triton X-100. Conditions: 7.5×10^{-8} M Eu^{3+}, 1.6×10^{-3} M TTA, 1×10^{-3} M DPG, 0.05 M NH_4Ac.

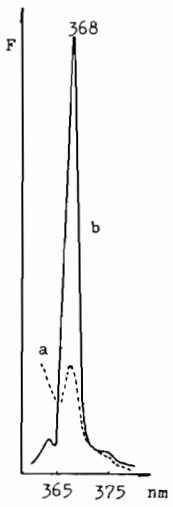

Fig. 3. Comparison between ternary and quaternary systems: (a) the Eu^{3+}–TTA–DPG system (Ex = 368 nm, factor = 30, 7.5×10^{-8} M Eu^{3+}); (b) the Eu^{3+}–TTA–DPG–Triton X-100 system (Ex = 368 nm, factor = 0.3, 7.5×10^{-8} M Eu^{3+}).

As an example, we compared Eu^{3+}–TTA–DPG with the Eu^{3+}–TTA–DPG–Triton X-100 system. Both of their excitation bands are at 368 nm, with fluorescence bands at 614.0 nm. However, in the presence of Triton X-100, the fluorescence intensity

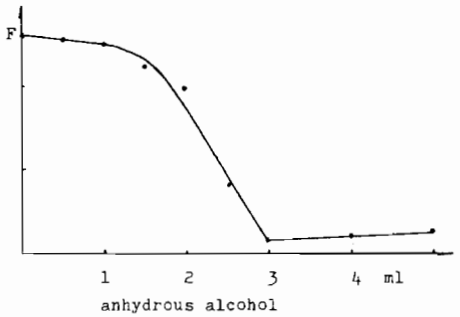

Fig. 4. Influence of the amount of ethanol on fluorescence. Conditions: 7.5×10^{-8} M Eu^{3+}, 1.6×10^{-4} M TTA, 1×10^{-3} M DPG, 0.05 M NH_4Ac, 0.125% Triton X-100.

TABLE II. Recovery of Sm, Eu and Tb

Sample	Known Eu (ng)	Element[a]	Taken	Found	Recovery (%)
Mixture		Sm	0.150	0.160	106.7
		Eu	2.0	2.2	110
		Tb	8.0	7.7	96.3
Mixture		Sm	0.075	0.080	106.7
		Eu	2.0	2.1	105
		Tb	4.0	3.8	95
Mixture		Sm	0.120	0.113	94.2
		Eu	2.5	2.7	108
		Tb	3.2	3.1	96.9
Gd_2O_3	2.1	Sm	0.375	0.390	104
		Eu	3.0	4.6	90.2
		Tb	8.0	7.8	97.5
Dy_2O_3	0.85	Sm	0.375	0.369	98.4
		Eu	3.0	3.95	102.6
		Tb	8.0	7.6	95
Nd_2O_3	1.0	Sm	0.375	0.353	94.1
		Eu	3.0	3.7	92.5
		Tb	8.0	7.5	93.8
La_2O_3	1.6	Sm	0.375	0.390	104
		Eu	3.0	5.0	108.7
		Tb	8.0	8.2	102.5
Er_2O_3	0.9	Sm	0.375	0.401	106.9
		Eu	3.0	3.6	92.3
		Tb	8.0	8.4	105
Lu_2O_3	2.4	Sm	0.375	0.369	98.4
		Eu	3.0	5.0	92.6
		Tb	8.0	8.0	100

[a]Sm and Tb measured in μg, Eu measured in ng .

increased appreciably and remained constant for several days, probably owing to formation of a micro-emulsion which decreases the transition energy and enhances the probability of the emission (see Fig. 3).

As a solvent, ethanol was used for dissolving organic reagents in this study. Figure 4 shows the variation of fluorescence of the ternary complex as a function of ethanol concentration. At first no variation was observed, and then the fluorescence decreased remarkably with the amount of ethanol. Perhaps the micellar of the complex was broken because of the presence of excess ethanol. The calibration graph is a linear function of concentration in the range of 1.0–5.0 ng of Eu, 0.075–0.45 μg of Sm and 1.6–20 μg of Tb per 10 ml.

In the system Ln^{3+}–TTA–DPG, the main interference comes from the other rare earth ions. The presence of Triton X-100 not only enhances the sensitivity but also decreases the interference. The results are listed in Table I.

This method was applied to the determination of Sm, Eu and Tb in rare earth oxides or artificially mixed samples. As can be seen from Table II, satisfactory results were obtained. The coefficient of variation was found to be *ca.* 0.4%.

References

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