

## Effect of Surfactant on Spectrofluorimetric Determination of Fe(III)

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In present studies, a simple and efficient spectrofluorimetric method has been described for trace determination of Fe(III). Method is based on quenching effect of traces of Fe<sup>3+</sup> on fluorescence intensity of Ce<sup>3+</sup> in the presence of TX-100 as a surfactant. The signal for Ce-Fe-TX-100 is monitored at  $\lambda_{\text{ex}} = 303.5$  nm and  $\lambda_{\text{em}} = 354$  nm. Optimum conditions were pH = 4, [TX-100] =  $8.33 \times 10^{-5}$  % v/v and 25 °C, which allows the determination of 0.2-15 µg/mL of Fe<sup>3+</sup> with limit of detection of 0.13 µg/mL. The quenching effects of some inorganic anions and cations were studied and showed there isn't serious interference. This system was chosen to develop a rapid and simple method for its determination of Fe<sup>3+</sup> in pharmaceutical formulation.

**Key Words:** Fe(III), Cerium(III), TX-100, Spectrofluorimetry, Determination.

### INTRODUCTION

The chemical properties of the transition metals are very similar. Consequently, it is difficult and important, to find specific reactions for individual ions, especially in their mixtures. Two types of methods have been adopted in fluorimetry determination of trace Fe<sup>3+</sup>. The methods based on the spectrofluorimetric techniques and electrochemical techniques such as: Extraction of iron(III) from sulphuric acid and hydrochloric acid solutions containing an excess of thiocyanate ions with tetraphenylphosphonium (TPP) chloride and cetyltrimethylammonium (CTMA) bromide in chloroform, selective determination of aluminum(III), iron(III) and titanium(IV) by ion-pair reversed-phase high-performance liquid chromatography, sequential determination of iron(II) and iron(III) in pharmaceutical by flow-injection analysis, using iron(III) chloride and 1,10-phenanthroline in determination of colchicines, Cloud point extraction of iron(III), determination of nonionic surfactants with iron(III) thiocyanate by using a PTFE membrane filter<sup>1-10</sup>. In this technique either Fe(III) was determined or it is used as reagent.

The interaction of cations with surfactants in aqueous solutions is of both considerable theoretical and practical importance and can have dramatic effects on the phase behaviour. Fluorescence, because of its high sensitivity, has become one of the most popular techniques of studying surfactant association in solution<sup>11</sup>. Lanthanide ions would appear to be good candidates for this. The association of lanthanide ions with surfactant aggregates also has other applications and implications. In addition, there is increasing interest in the mesomorphism of lanthanide salts of anionic amphiphiles<sup>12-14</sup>.

In this paper the quenching effect of Fe(III) on Ce(III) ion fluorescence intensity in presence of surfactant are reported and a very simple and efficient method for the determination of trace amounts of Fe(III) in solution is described.

## EXPERIMENTAL

The fluorimetric measurements were carried out on a Perkin-Elmer LS50 Luminescence spectrophotometer with a 150 W Xenon arc lamp. Instrumental parameters and processing data were controlled by the Fluorescence Data Manager software (FL WINLAB). All measurements were performed with 1 cm thick spectrofluorimetric cells for batch procedure at room temperature by use of a thermostatic cell holder and a Selecta Unitronic 320 OR thermostatic water-bath. The excitation and emission slit widths were 10 and 2.5 nm, respectively. A Jenway 3510 pH meter was used for pH measurements.

Highest grade commercially available reagents were used throughout this study without further purification. Doubly distilled water was employed for all dilutions. Cerium(III) stock solution ( $1.0 \times 10^{-3}$  M) was prepared by dissolving 0.0434 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Merck) into a 100 mL flask and diluting to the mark with water. Working solutions of  $\text{Ce}^{3+}$  were prepared by appropriate dilution with water. Surfactant solution 0.5 % (v/v) was prepared by dissolving 0.5 mL of any surfactant (Merck) into a 100 mL volumetric flask and then diluting to the mark.

Buffer solution was prepared by dissolving 1.5457 g boric acid in water and adjusting the pH with  $0.1 \text{ mol L}^{-1}$  sodium hydroxide and hydrochloric acid solution to give a final total volume of 250 mL.

Fe(III) solutions  $1000 \mu\text{g/mL}$  were prepared daily by dissolving 0.180 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck) in doubly distilled water in 25 mL volumetric flask. Standard solutions were prepared daily from the stock solution by serial dilution with water.

**Procedure:** Apparent fluorescence excitation and emission spectra were measured at room temperature and optimum excitation and emission wavelengths and slit widths were found from these spectra.

A known amount of Ce(III), Fe(III) and Triton X-100 were placed in 3 mL quartz cell, respectively. Next, 1 mL buffer (pH = 4) was added and the mixture was diluted with water in order to desired concentration and volume. The cell was shaken vigorously and immediately the excitation and emission spectra were recorded at 303.5 and 354 nm, respectively. The excitation and emission slit widths were registered in 10 and 2.5 nm, respectively.

## RESULTS AND DISCUSSION

**Fluorescence spectra:** In primary researches it was noted that the Fe(III) ion decreases fluorescence intensity of Ce(III). Fig. 1 shows decreasing in the excitation and emission fluorescence spectra of Ce(III) ion in presence of Fe(III) with constant emission and excitation wavelengths ( $\lambda_{\text{em}} = 354$ ,  $\lambda_{\text{ex}} = 303.5$ ), respectively.

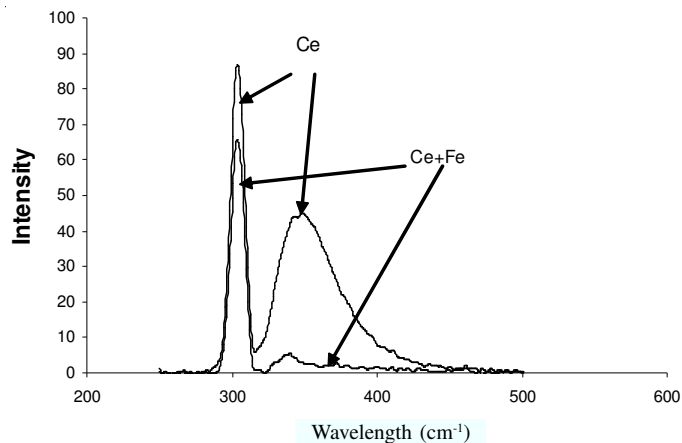


Fig. 1. Excitation and emission spectra of 10 µg/mL Ce(III) ion in presence of Fe(III) ion ( $\lambda_{em} = 354 \text{ nm}$ ,  $\lambda_{ex} = 303.5 \text{ nm}$ )

**Influence factors on the fluorescence intensity of the system:** Decreasing of Ce(III) fluorescence intensity in this system related to different parameters were optimized. The enhanced fluorescence intensity was represented as  $\Delta F = (F - F_0)$  where, F and  $F_0$  were the fluorescence intensities of sample and blank, respectively.

**Effect of Ce(III) concentration:** Effect of Ce(III) concentration on system fluorescence intensity were studied in ranges of 1-25 µg/mL with 2 µg/mL Fe(III). As seen from Fig. 2 the optimum of Ce(III) concentration was selected 10 µg/mL.

**Effect of pH:** The effect of pH on the fluorescence intensity of the system was studied (Fig. 3). The pH effect was studied in the range 1-10.

Effects of 0.2, 0.5, 0.7, 1, 1.2, 1.5 mL of buffer were studied on fluorescence intensity of Ce(III). For 1 mL obtained increasing of repeatability and as can be seen when volume was increased had no influence, so 1 mL was selected for further research.

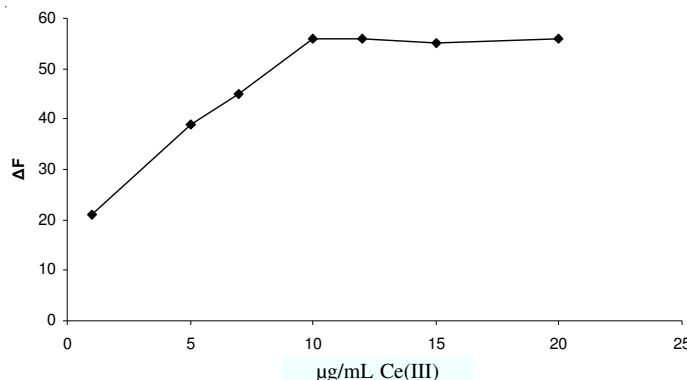


Fig. 2. Effect of Ce(III) concentration in presence of 2 µg/mL Fe(III) ( $\lambda_{em} = 354 \text{ nm}$ ,  $\lambda_{ex} = 303.5 \text{ nm}$ )

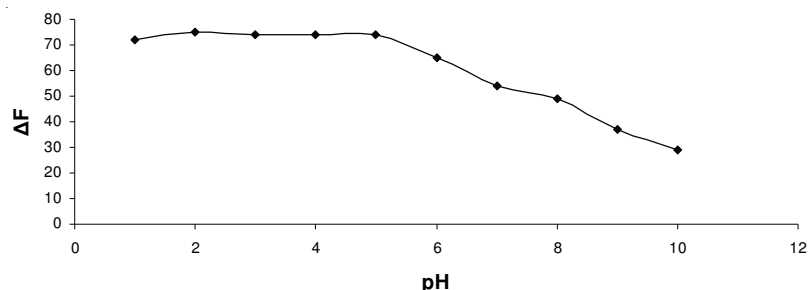


Fig. 3. Effect of pH 10  $\mu\text{g/mL}$  Ce(III) in presence of 2  $\mu\text{g/mL}$  Fe(III) and TX-100 (8.33 % v/v) ( $\lambda_{\text{em}} = 354 \text{ nm}$ ,  $\lambda_{\text{ex}} = 303.5 \text{ nm}$ )

From Fig. 3, it could be seen that  $F$  remained constant with an increase in pH lower than 5, when pH was up, it decreased.

The above results could be explained as follows:  $\text{Ce}^{3+}$  fluorescence enhancement might be up with TX-100, obviously, it was advantageous of TX-100 coordinating in the acidic environment.

The results indicate that the changes of pH would influence the fluorescence intensity. So, the optimum pH range is 2-5, a pH of 4.0 was chosen for further research.

**Effect of surfactants:** Surfactants were frequently employed to solubilize hydrophobic compounds as well as to increase the fluorescence intensities of weakly fluorescent compounds, because micellar solutions could improve the microenvironment of luminescence. The experiments indicated that the surfactants had a large effect on the fluorescence intensity of the system. Under the same condition, the following surfactants were tested *viz.*, sodium dodecyl benzene sulphonate (SDBS), sodium dodecyl sulphate (SDS), Triton X-114 (TX-114), Triton X-100 (TX-100), N cetyl pyridinium chloride (NC-Cl) and N cetyl pyridinium bromide (NC-Br). From Table-1, it was found that different kinds of surfactants could increase the fluorescence intensity of the system to different extents and the most effective surfactant was TX-100 (Table-1).

TABLE-1  
EFFECT OF SURFACTANTS ON Fe(III) AND Ce(III) MIXTURE

Surfactant	SDBS	SDS	TX-114	TX-100	NC-Cl	NC-Br
$\Delta F$	30	32	48	75	19	14

**Effect of surfactant concentration:** The effect of TX-100 concentration on the fluorescence intensity of the system had also been studied the results are shown in Fig. 4. The wavelengths were fixed and  $\Delta F$  vs. TX-100 concentration was studied. From this Fig. 4, found that fluorescence intensity enhanced with concentration then constant. So, the TX-100 concentration of  $8.33 \times 10^{-5} \text{ \%v/v}$  was selected for further research.

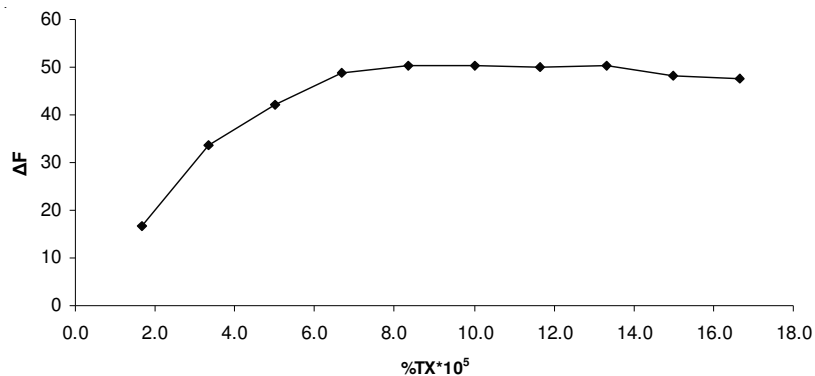


Fig. 4. Effect of (% v/v) TX-100 on 10  $\mu\text{g/mL}$  Ce(III) ion fluorescence intensity in presence of 2  $\mu\text{g/mL}$  Fe(III) and TX-100 (8.33 %v/v), pH=4. ( $\lambda_{\text{em}} = 354 \text{ nm}$ ,  $\lambda_{\text{ex}} = 303.5 \text{ nm}$ )

**Effect of temperature:** The influence of the temperature was studied between 5 to 55  $^{\circ}\text{C}$ . From Fig. 5, it could be observed that the temperature effect is not pronounced between 10 to 50  $^{\circ}\text{C}$  and room temperature (25  $^{\circ}\text{C}$ ) is recommended.

**Effect of ionic strength:** Excitation and emission spectra of Fe(III)-Ce(III) in 1 M potassium nitrate were recorded. It could be observed that increase of ionic strength had no influence on the fluorescence intensity, whereas no potassium nitrate was added.

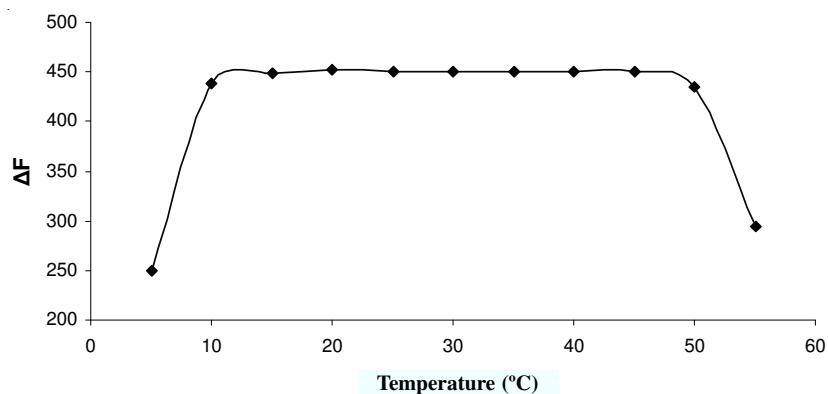


Fig. 5. Effect of temperature on 10  $\mu\text{g/mL}$  Ce(III) ion fluorescence intensity in presence of 2  $\mu\text{g/mL}$  Fe(III) and TX-100 (8.33 % v/v), pH = 4 ( $\lambda_{\text{em}} = 354 \text{ nm}$ ,  $\lambda_{\text{ex}} = 303.5 \text{ nm}$ )

**Calibration curve and analytical parameters:** Under the optimum physico-chemical conditions, the fluorescence intensity was measured at  $\lambda_{\text{ex}} = 303.5 \text{ nm}$  and  $\lambda_{\text{em}} = 354 \text{ nm}$ . The calibration graph for the determination of Ce(III) was constructed under the optimum conditions. Excellent linearity were obtained over the range between 0.2-15  $\mu\text{g mL}^{-1}$ .

TABLE-2  
STATISTICAL PARAMETERS FOR THE SPECTROFLUORIMETRIC  
DETERMINATION Fe(III) IN PRESENCE OF TX-100

LDR	Correlation coefficient	DL
0.2-15 µg/mL	0.9998	0.13 µg/mL

**Interferences of common metal ions and anions:** Under optimum conditions, interferences of foreign metal ions on the fluorescence intensity of the system were studied. Most of the ions did not interfere with the determination when their concentrations were not high enough.

**Application of the method:** The procedure was applied to the determination of trace amounts of Fe(III) in real samples with good accuracy being achieved. The mean of recovery percentages were  $98.93 \pm 1.4 \%$  and there was no interference. The results indicate that the proposed method is suitable and can be successfully applied.

### Conclusion

From the results obtained, it can be concluded that this work is a very simple and efficient method for trace determination of Fe(III). The advantage of this technique is caused the method have both high sensitivity and repeatability.

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