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Spectrofluorimetric Method for Trace Determination of Ce(III) in Presence of Surfactant Triton-X-100

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A simple, efficient and feasible spectrofluorimetric method has been developed for trace determination of cerium(III). The use of surfactant Triton-X-100 (TX100) was investigated. The fluorescence intensity of Ce^{3+} was enhanced when 1.16×10^{-6} % (v/v) of TX100 was added and it was measured by a 1 cm quartz cell with luminescence spectrometer at room temperature. The apparent wavelengths were $\lambda_{ex} = 303.5$ nm and $\lambda_{em} = 354$ nm. The enhanced fluorescence intensity of the system (ΔF) showed 2 linear relationships with the concentration of Ce^{3+} in the ranges of 50-800 ng/mL and 5-30 μg/mL and correlation coefficient 0.9997 and 0.9996, respectively. The detection limit (S/N = 3) of Ce^{3+} was 18.70 ng/mL. The influence parameters such as surfactant concentration, pH, temperature and ionic strength were optimized. The quenching effects of some inorganic anions and cations were studied and showed there isn't serious. The presented method was used to determine Ce^{3+} in synthetic samples, which give satisfactory results.

Key Words: Cerium(III), TX100, Spectrofluorimetry method.

INTRODUCTION

The chemical properties of the rare earth elements are very similar. Consequently, it is difficult and important, to find specific reactions for individual ions, especially in their mixtures. Two types of methods, direct and indirect methods have been adopted in fluorimetry determination of traces of Ce^{3+}. The direct methods based on the ultraviolet fluorescence of Ce^{3+} ions in strongly acidic media or in some organic ligand solutions[1-7], while in the indirect methods, fluorescence of some organic molecules are affected by the presence of Ce^{3+} ions, such as the decomposition of 2-[(8-hydroxy-5-sulpho-7-quinonyl)azo]-1,8-dihydroxy naphthalene-3,6-disulphonic acid[8] with Ce^{3+} and oxidative reaction of Ce^{4+} with some organic reagents[9]. Mostly, the direct methods are more sensitive than the indirect ones[6]. However, interference from coexist ions, especially for some rare earth ions, Fe^{3+} and PO_4^{3-} are always faced in the direct methods.

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[10]. Lanthanide ions would appear to be candidates for this object. 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[11-14].

It is found that TX100 acts as a specific reagent for enhancing the fluorescence intensity of Ce(III) in aqueous solutions. In this study, the fundamental conditions for the determination of Ce(III) with TX100 solution by using fluorescence spectroscopy were described. Furthermore, from results of these studies, it is shown that this procedure is effective for the spectrofluorimetric determination of Ce(III).

EXPERIMENTAL

Highest grade commercially available reagents were used throughout the study without further purification. Doubly distilled water was employed for all dilutions. Cerium(III) stock solution (1.0×10^{-3} M) was prepared by dissolving 0.0434 g of $Ce(NO_3)_3.6H_2O$ (Merck) into a 100 mL flask and diluting to the mark with water. Standard solutions were prepared daily from the stock solution by serial dilution with water. Working solutions of Ce^{3+} were prepared by proper 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 mol L^{-1} sodium hydroxide and hydrochloric acid solution to give a final total volume of 250 mL at pH 4.

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 and the use of a thermostatic cell holder and a Selecta Unitronic 320 OR thermostatic water-bath for maintaining temperature. A Jenway 3510 pH meter was used for pH measurements.

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) 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 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

Fig. 1 shows the excitation and emission fluorescence spectra of Ce(III) ion in constant emission and excitation wavelengths (λ_{em} = 354 nm, λ_{ex} =303.5 nm), respectively.

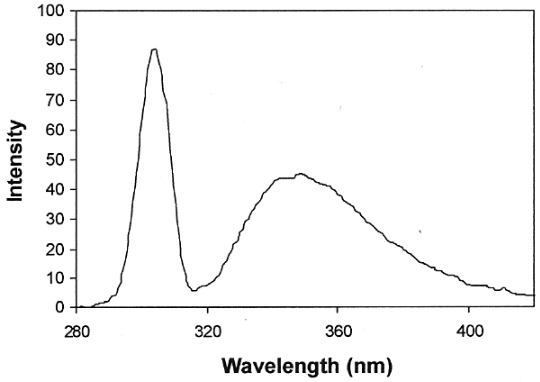

Fig. 1. Excitation and emission spectra of 10 μg/mL Ce(III) (λ_{em} = 354 nm, λ_{ex} = 303.5)

Influence factors on the fluorescence intensity of the system

Type of surfactants: Surfactants were often employed to soluble 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 the surfactants had a large effect on the fluorescence intensity of the system. Under the same condition, the following surfactants were tested: SDBS, SDS, TX-114, TX-100, N cetyl pridinium chloride (NC-Cl) and N-cetyl pridinium bromide (NC-Br). The results are shown in Table-1, that enhanced fluorescence intensity was represented as $\Delta F = F\text{-}F_0$. Here, F_0 to F were the fluorescence intensities of blank and sample solutions, respectively. 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 TX100.

TABLE-1
EFFECT OF SURFACTANTS ON THE FLUORESCENCE INTENSITY OF THE SYSTEM

Surfactant	TX 114	TX 100	NC-Cl	NC-Br	SDBS	SDS
ΔF	71	111	2.7	2.5	31	41

Effect of surfactant concentration: Fig. 2 shows the excitation and emission spectra of 1 μg/mL Ce(III) ion in various concentrations of Triton-X-100 solution. Maximum excitation and emission wavelengths are observed at 303.5 and 354 nm, respectively.

The effect of TX100 concentration on the fluorescence intensity was studied, the results are shown in Fig. 3. It shows, ΔF increased with concentration of TX 100 up to 11.6×10^{-5} % (v/v) and more concentration has no change on fluorescence intensity. So, the TX100 concentration of 11.6×10^{-5} % (v/v) was selected for further study.

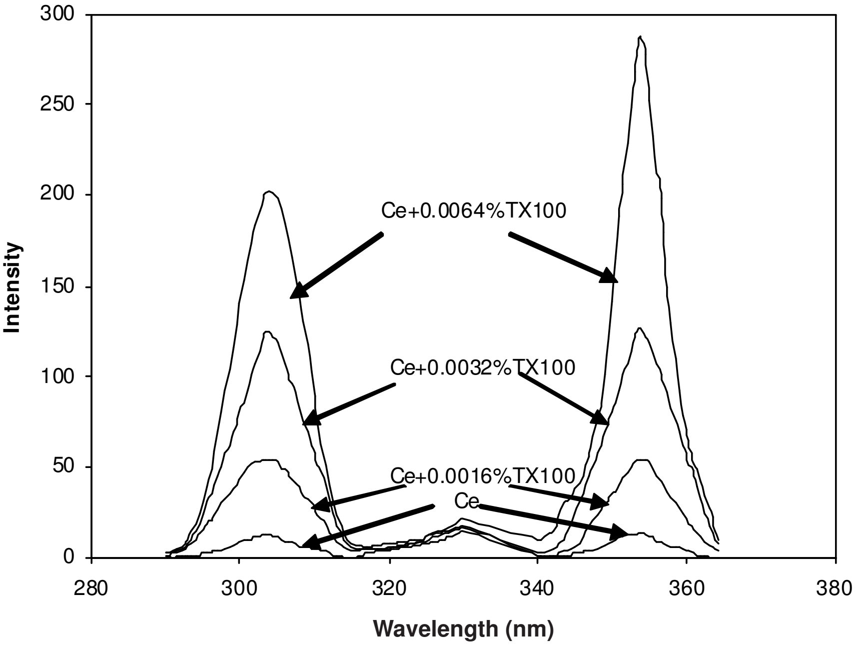

Fig. 2. Excitation and emission spectra of 1 μg/mL Ce(III) ion in various concentrations of (% v/v) Triton-X-100

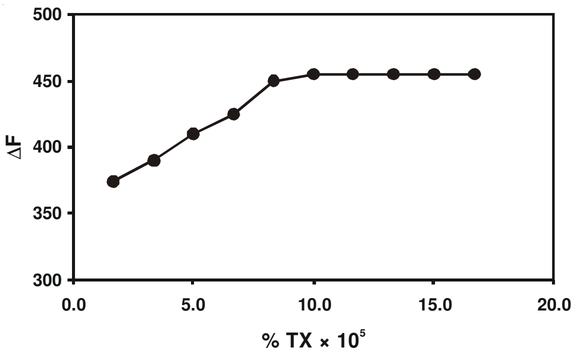

Fig. 3. Effect of (% v/v) TX100 on fluorescence intensity of 10 μg/mL Ce(III) ion (λ_{em} = 354 nm, λ_{ex} = 303.5 nm)

Effect of pH and buffer volume: The selection of pH is important for the fluorescence characters. Effect of pH on the fluorescence intensity of the system was studied, by addition of suitable amount of HCl and NaOH 0.1 M and adjustment by pH meter. The pH effect was studied in the range 1-10. From Fig. 4, it could be seen that ΔF remained constant with an increase in pH is lower than 5, when pH is higher, then it decreased. The above results could be explained as follows:

Ce^{3+} fluorescence enhancement might was up with TX100, obviously, it was helpful of TX100 coordinating in the acidic media. The results indicate the changes of pH would influence the fluorescence intensity. So, the best pH range is 2-5, a pH of 4.0 was chosen for further study.

The buffer solution of boric acid was used for adjusting of pH = 4.0. The effect of volumes of buffer 0.2, 0.5, 0.7, 1, 1.2, 1.5 mL of its were studied on fluorescence intensity of Ce(III). To increase of buffer volume up to 1 mL, the reproducibility enhanced and the higher volume buffer has no influence, so 1 mL was selected for further research.

Effect of temperature: The influence of the temperature was studied between 5 to 55 ºC. It could be observed from Fig. 5, temperature effect is not pronounced between 10 to 50 ºC and so room temperature (25 ºC) is recommended.

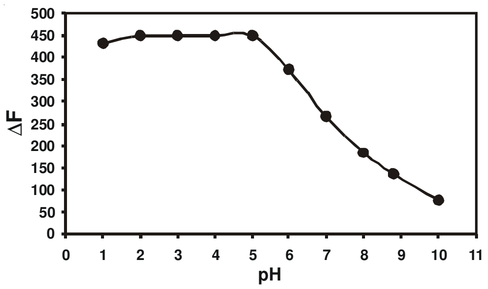

Fig. 4. Effect of pH on fluorescence intensity of 10 μg/mL Ce(III) ion. (TX100 = 11.6 × 10^{-5} % v/v)

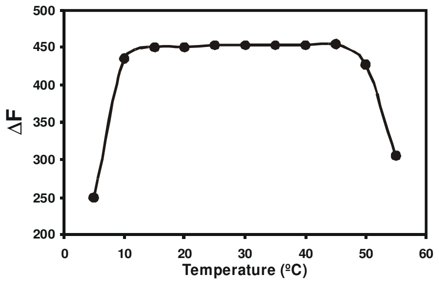

Fig. 5. Effect of temperature on fluorescence intensity of 10 μg/mL Ce(III) ion. (TX100 = 11.6 × 10^{-5} % v/v, pH = 4)

Effect of ionic strength: Excitation and emission spectra of Ce(III) in 1 M potassium nitrate were considered. It could be observed that increase of ionic strength until 0.5 M KNO_3 had no influence on the fluorescence intensity.

Calibration curve and analytical parameters: Under the optimum physicochemical conditions, the fluorescence intensity was measured at λ_{ex} = 303.5 nm and λ_{em} = 354 nm. Two calibration graphs for the determination of Ce(III) were obtained. Linearity were resulted over the range between 5-30 μg mL^{-1} and 50-800 ng mL^{-1} of Ce(III). The limit of detection is 18.70 ng/mL. The statistical parameters for the spectrofluorimetric determination of Ce(III) in the presence of TX100 were shown in Table-2.

TABLE-2
STATISTICAL PARAMETERS FOR THE SPECTROFLUORIMETRIC DETERMINATION OF Ce(III) IN PRESENCE OF TX100

LDR	Equation	Correlation coefficient	DL
5-30 μg/mL	$\Delta F = 23.1060C^{a}_{Ce(III)} + 231.84$	0.9996	–
50-800 ng/mL	$\Delta F = 0.2004C^{b}_{Ce(III)} + 0.3582$	0.9997	18.70 ng/mL

C^a = Concentration of Ce(III) in μg/mL; C^b = Concentration of Ce(III) in ng/mL.

Effect of interfacing ions: Under optimum conditions, interferences of foreign metal ions and anions on the fluorescence intensity of the system were studied. At a Ce(III) concentration of 200 ng/mL, the highest permissible molar excesses of the foreign ions causing a ± 10 % relative error in the fluorescence intensity were more than 200-fold molar excess of Mg^{2+} and Zn^{2+} and 50-fold molar excess of Cu^{2+} and Ca^{2+}. Fe^{3+} and Al^{3+} are interference ions that were removed with 0.01 M of F^{-}. Therefore, these ions did not interfere with the determination when their concentrations were not high. By the way, we have also no serious anions interference.

Application of the proposed method: The procedure was applied to determine trace amounts of cerium(III) in some synthetic mixtures with good recovery being achieved (Table-3). The results indicate the proposed method is suitable and can be successfully applied for determination of Ce(III).

TABLE-3
RECOVERIES OBTAINED WITH THE PROPOSED SPECTROFLUORIMETRIC METHOD IN SYNTHETIC SAMPLES[a]

Sample No.	Ce(III) added (ng/mL)	Ce(III) found	Recovery (%)	Sample No.	Ce(III) added (µg/mL)	Ce(III) found	Recovery (%)
1	50.0	49.0	98.0	6	5.2	5.1	98.1
2	120.0	122.0	101.6	7	10.0	10.2	102.0
3	250.0	246.0	98.4	8	20.0	20.5	102.5
4	400.0	410.0	102.5	9	25.0	24.7	98.8
5	750.0	756.0	100.8	10	30.0	29.8	99.3

[a] It contains: WO_4^{2-} (0.5 µg/mL), Cr^{3+}, Ni^{2+}, Sr^{3+}, Mn^{2+} (1.0 µg/mL) Hg^{2+}, CN^{-} (3.0 µg/mL) SO_3^{2-}, PO_4^{3-} (10.0 µg/mL).

Conclusion

The method was found to be a perfect economic spectrofluorimetric determination method of cerium(III) with high sensitivity and wide linear range. The advantage of this technique is caused by the fluorescence enhancing effect and the high stability of Ce-TX100, which made the method have both applicability and repeatability.

REFERENCES

1. B. Herber, *Nature*, **222**, 161 (1969).
2. G.F. Kirbright, C.G. Saw and T.S. West, *Talanta*, **16**, 65 (1969).
3. Z. Yulun, *Yanshi Kuangwu Ji Ceshi*, **3**, 344 (1984).
4. P. Cukor and R.P. Weberling, *Anal. Chim. Acta*, **41**, 404 (1968).
5. C.T. Hjeu, A.I. Volkovs and T.E. Getman, *Zh. Anal. Khim.*, **24**, 688 (1969).
6. A. Akseli and Y. Rakicioglu, *Talanta*, **43**, 1983 (1996).
7. A. Akseli and Y. Rakicioglu, *Fresenius J. Anal. Chem.*, **354**, 424 (1996).
8. Y. Yuan, J. Zhiqin and H. Jianfeng, *Fenxi Huaxue*, **21**, 53 (1993).
9. B.K. Pal, F. Toneguzzo and A. Corsini, *Anal. Chim. Acta*, **88**, 353 (1977).
10. M.J. Tapia, D. Burrows and M. Emilia, *Phys. Chem. B*, **106**, 966 (2002).
11. W.A. Armstrong, D.W. Grant and W. Humpreys, *Anal. Chem.*, **35**, 1300 (1963).
12. P. Ghosh, A.D. Shukla and A. Das, *Tetrahedron Lett.*, **43**, 7419 (2002).
13. G.F. Kirkbright, C.G. Saw and T.S. West, *Talanta*, **16**, 65 (1969).
14. J. Nianqin, Y. Jinghe and L. Tao, *Talanta*, **41**, 415 (1994).

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