Spectrofluorimetric Determination of Oxalate Based on Its Ternary Complex between Eu^{3+} and Thenoyltrifluoroacetone

Ki Won Cha,* Hua Zi Huang, and Hyun Cheol Choi

Department of Chemistry, Inha University, Incheon 402-751, Korea
Received July 22, 2002

A simple, sensitive and selective determination method of oxalate has been investigated based on the fluorescence enhancement of Eu^{3+}-TTA complex due to the formation of Eu^{3+}-TTA-oxalate ternary complex. An emission peak of Eu^{3+}-TTA, which is increased linearly with addition of oxalate, occurs at 610 nm in aqueous solution with excitation at 306 nm. The linear range of the calibration curve is 1×10^{-6}- 8×10^{-6} M and the detection limit is 1×10^{-6} M. The effects of foreign ions were studied. The present method was applied to determine oxalate of two synthetic samples.

Key Words : Oxalate, Eu^{3+}, Thenoyltrifluoroacetone (TTA), Fluorescence, Enhancement

Introduction

Oxalate is one of important nutrients in the human diet found principally in spinach, beet leaves, etc. Oxalate is primary chelator of calcium ion, so it forms chelates with dietary calcium, thus gives the complex unavailable for adsorption in the body and absorbed oxalate causes also to be precipitated as insoluble salts that accumulate in the renal tissue. So calcium oxalate is a most important phase in case of stone diseases.[1] Therefore, the determination of oxalate in the some biological material is important.

Several determination methods of oxalate such as spectrophotometric,[2] amperometric,[3-6] spectrofluorimetric,[7] chemiluminescence method[8] have been proposed. However, those methods have no sufficient sensitivity. Other methods such as isotope dilution mass spectrometry,[9] differential pulse polarography,[15] chromatography[10-12] are also used for oxalate determination but those methods are required special instrumentation and relatively high cost of analysis. So a simple, sensitive and inexpensive determination method of oxalate is required. Luminescence of lanthanide complex has been applied to the determination of lanthanide ions[16-17] and we found that the fluorescence intensity of Eu^{3+}-TTA complex changed in the addition of some organic compounds. For example, phosphate decreased the fluorescence intensity of the complex,[13] but glycine increased the fluorescence intensity of the complex,[14] which were applied to the determination of those ions. We investigated the determination method of oxalate using the increase of the fluorescence intensity of Eu^{3+}-TTA complex added to oxalate.

Experimental Section

Apparatus and Reagents. The fluorescence intensity measurements were done with a Shimatzu RF- 5301 PC spectrofluorophotometer, using 1 cm quartz cell. The band passes were 10 nm for excitation and emission monochrometers. The light source was a 150 w xenon lamp. Voltammograms were measured with CV-50W voltammetric analyzer (BAS). All pHs were measured with a Mettler Talodo MP 220 pH meter.

Europium oxide (99.95%) was obtained from Aldrich Co.. Stock solution of the europium ion was prepared by dissolving a known amount of the europium oxide in hydrochloric acid. Standard solution of it were prepared by further dilution with water. Stock solution of TTA (1×10^{-3} M) was prepared by dissolving TTA in 30% ethanol. The working standard solution of oxalate were prepared by diluting a 1.0×10^{-3} M $Na_2C_2O_4$ stock solution. Hexamethylenetetramine (hexamine, 1.0 M) was prepared as a buffer solution and the pHs adjusted to 6.5 with hydrochloric acid. Analytical chemicals and deionized distilled water were used throughout the experiment.

Procedure. To a 50 mL volumetric flask, 5 mL of pH 6.5 buffer solution, 2.5 mL of 1.0×10^{-4} M TTA, 1.0 mL of 1.0×10^{-4} M Eu^{3+} and 5.0 mL of 1.0×10^{-4} M oxalate were added and diluted to the mark with water. The fluorescence intensity of the solution was measured at 610 nm with a excitation wavelength at 306 nm. All fluorescence intensity was corrected with blank solution (Eu^{3+}-TTA) and all experiments were conducted at room temperature (25 °C).

Results and Discussion

Excitation and emission spectra. The excitation and emission spectra of the Eu^{3+}-TTA-oxalate system are shown in Figure 1. In Figure 1, the maxium excitation and emission wavelength were 306 nm and 610 nm, respectively. The a and a' curves are the excitation spectra of Eu^{3+}-TTA and Eu^{3+}-TTA-oxalate and b and b' curves are the emission spectra of the same, respectively. The presence of oxalate resulted in an increase of the absorbance and emission intensity but no chnge in the maxium wavelength.

The pH effects on the relative fluorescence intencity of Eu^{3+}-TTA-oxalate was studied in the range of pH 3-9 (Figure

*Corresponding Author: Fax +82-32-872-2520, e-mail: kwcha@inha.ac.kr

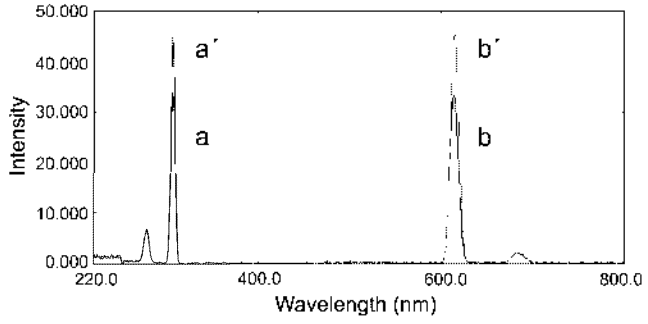

Figure 1. Excitation (a and a') and emission (b and b') of Eu(III)-TTA complex in the absence (a, b) and presence (a', b') of oxalate. Eu(III): 2×10^{-6} M, TTA: 6×10^{-6} M, Oxalate: 1×10^{-5} M.

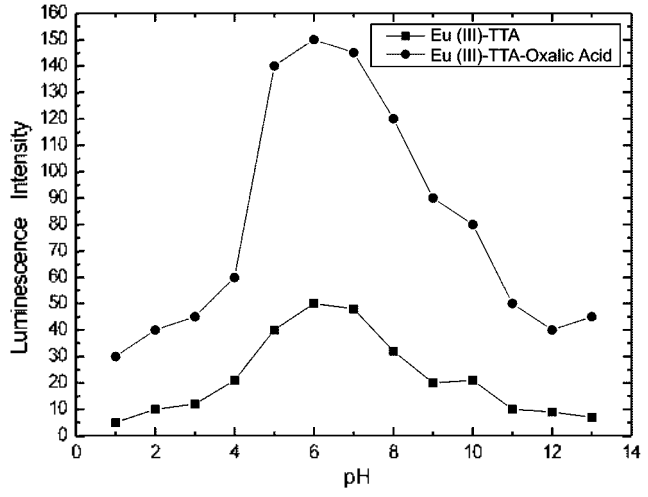

Figure 2. pH effects on the fluorescence intensity of Eu(III)-TTA and Eu(III)-TTA-oxalate. Eu(III): 2×10^{-6} M, TTA: 6×10^{-6} M, Oxalate: 1×10^{-5} M.

2). The results indicate that the maxium fluorescence intensity was obtained at pH 5-8 of hexamethylenetetramine-HCl buffer. Thus, pH 6.5 hexamine buffer solution was recommended for the further examination. This pH improved the stability of the complex. The concentration effects of TTA and Eu^{3+} on the fluorescence intensity of Eu^{3+}-TTA-oxalate system was also studied. The fluorescence intensity increased with the increase in TTA concentration to 6×10^{-6} M in the presence of 2×10^{-6} M Eu^{3+} and decrease at the higher concentration. The fluorescence intensity of Eu^{3+}-TTA-oxalate system was influenced by the concentration of TTA and Eu^{3+}. Therefore, these concentration must retained constantly to determine oxalate. The composition of the Eu^{3+}-TTA-oxalate system was investigated. The mole ratio between Eu^{3+} and TTA was 1 : 3 and the mole ratio between Eu^{3+} and oxalate was 1 : 2. Therefore, the composition of the complex was $Eu^{3+}(TTA)_3(oxalate)_2$.

Enhancement mechanism: The fluorescence intensity of Eu^{3+} is weak due to the low oscillatory strength of its absorption.[18] But a fluorescence enhancement of Eu^{3+} could be achieved by energy transfer from the triple state of organic ligand to the Eu^{3+} in the complex. This energy transfer is called intramolecular energy transfer.[18-20] The composition

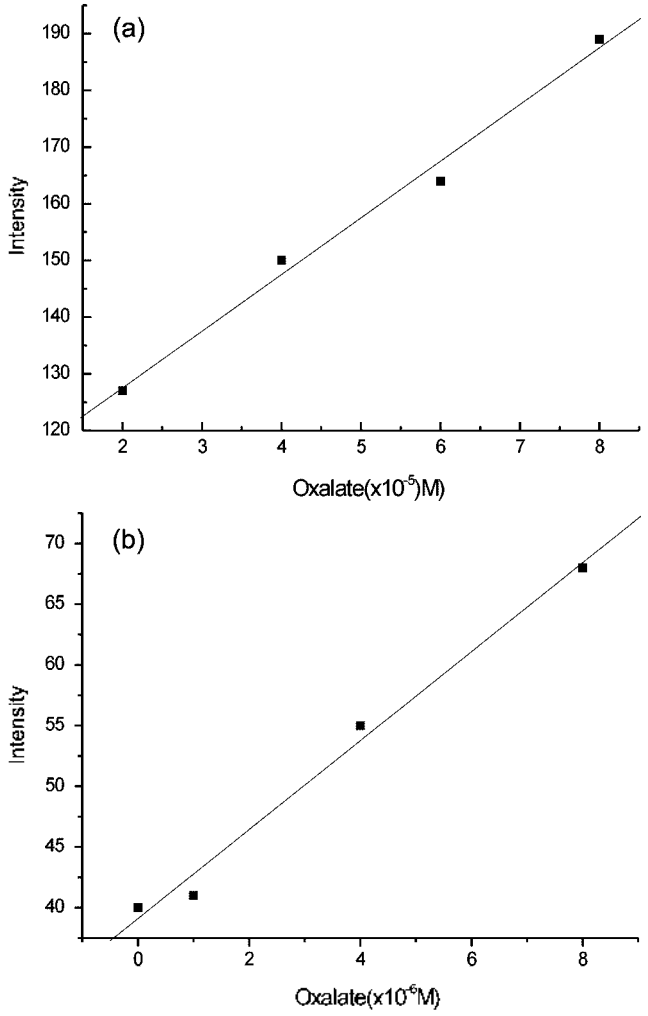

Figure 3. Calibration curves of oxalate.

of Eu^{3+}-TTA chelate is $Eu^{3+}(TTA)_3(H_2O)_2$.[11] In the presence of oxalate ion , the structure of the chelate include two oxalate ions instead of two water molecules and the oxalate ion prevents the quenching by water molecules, which probably act the vibration of the O-H bond.[21] Therefore, the fluorescence intensity of Eu^{3+}-TTA will be increased with addition of oxalate.

Calibration curves of oxalate. The increase of the fluore-

Table 1. Tolerance limits of foreign ions

Ions	Tolerance
acetate	1×10^{-4} M
benzoate	2×10^{-4} M
citrate	4×10^{-4} M
CO_3^{2-}	5×10^{-4} M
SO_4^{2-}	2×10^{-4} M
BO_3^{3-}	8×10^{-3} M
CrO_4^{2-}	1×10^{-5} M
SiO_3^{2-}	1×10^{-5} M
Ca^{2+}	3×10^{-4} M
Mg^{2+}	7×10^{-4} M

Eu^{3+}: 2×10^{-6} M, TTA: 6×10^{-6} M, pH = 6.5, Oxalate: 2×10^{-5} M.

Table 2. Composition of synthetic sample and analytical data

	Composition	Present	RSD	Polarography
No 1	1×10^{-5} M of acetate, benzoate, citrate, carbonate, sulfate, Ca^{2+} and Mg^{2+} in 2.00×10^{-6} M oxalate	1.98×10^{-6} M	2.1% (N=3)	2.15×10^{-6} M
No 2	1×10^{-5} M of acetate, benzoate, citrate carbonate, sulfate, Ca^{2+} and Mg^{2+} in 2.00×10^{-5} M oxalate	2.12×10^{-5} M	3.2% (N=3)	2.80×10^{-5} M

scence intensity of the Eu^{3+}-TTA -oxalate complex was a linear function of oxalate concentration. The linear range was 1×10^{-5}~8×10^{-5} M oxalate concentration when the concentration of Eu^{3+} and TTA was 2×10^{-6} M and 6×10^{-6} M, respectively (r = 0.9994) and was 1×10^{-6}~8×10^{-6} M when the concentration of Eu^{3+} and TTA was 2×10^{-7} M and 6×10^{-6} M, respectively (r = 0.9946). The detection limit was 1.0×10^{-7} M oxalate (S/N = 3).

Interference. The effects of some anions and cations on the fluorescence intencity of Eu^{3+}-TTA-oxalate complex were investigated in the presence of 2×10^{-5} M oxalate (Table 1). The tolerance limits was calculated by the concentration of foreign ions, resulting in less than 5% deviation of the fluorescence intensity of Eu^{3+}-TTA in the 2×10^{-5} M oxalate. In Table 1, most anions have a relatively high tolerance limit, except silicate and chromate ion.

Application. To study the validity of the present method, two synthetic samples were prepared and oxalate content was determined by present method and differential pulse polarography after derivatization of oxalate with *o*-phenylenediamine.[15] The analytical data obtained by the standard addition method of present method was compared with the results of differential pulse polarography (Table 2). In two data good agreement was obtained as seen in Table 2.

Conclusion

A simple, sensitive and selective determination method of oxalate was studied using the fluorescence enhancement of Eu^{3+}-TTA complex. The fluorescence intensity of Eu^{3+}-TTA complex was increased linearly with addition of oxalate in the concentration range 1×10^{-6}~8×10^{-6} M. The present method was applied to determine oxalate content in a synthetic samples.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2001-015-DP0290).

References

1. Zhang, Z. Q.; Xu, X. Q. *Anal. Chim. Acta* **2000**, *406*, 303.
2. Infants, J. A.; Luque, M. D.; Valcarcel, M. *Anal. Chim. Acta* **1991**, *242*, 179.
3. Fogg, A. G.; Alonso, R. M.; Fenandez, M. A. *Analyst* **1986**, *111*, 249.
4. Alnnaibd, A. M.; Townhend, A. *Anal. Chim. Acta* **1989**, *218*, 1.
5. Leon, L. E.; Rois, A.; Luque, M. D.; Valcarcel, M. *Analyst* **1990**, *115*, 1549.
6. Leon, L. E.; Rois, A.; Luque, M. D.; Valcarcel, M. *Anal. Chim. Acta* **1990**, *234*, 227.
7. Perez-Raiz, T.; Martinez, C.; Tomas, V.; Casajus, R. *Analyst* **1995**, *120*, 2111.
8. Perez-Raiz, T.; Martinez, C.; San, A.; Val, V. *Anal. Chem. Acta* **1993**, *284*, 1973.
9. Zara, A. J.; Bulbore, L. O. *Anal. Lett.* **1987**, *20*, 213.
10. Chen, Y.; Li, Q.; Yang, Z.; Zhang, F. *Chiniese J. Chromatogr.* **1989**, *7*, 226.
11. Utzman, S. *J. Chromatogr.* **1993**, *640*, 282.
12. Brega, A.; Quadri, A. *J. Liq. Chromatogr.* **1992**, *15*, 501.
13. Cha, K. W.; Park, C. I.; Jung, Y. B.; Park, K. W. *Bull. Korean Chem. Soc.* **2000**, *21*, 529.
14. Cha, K. W.; Park, C. I.; Park, K. W. *Bull. Korean Chem. Soc.* **2002**, *23*, 623.
15. Jose, A. R.; Aquiles, A. B. *Anal. Chim. Acta* **1993**, *273*, 531.
16. Jianzhong, L.; Zhujun, Z. *Anal. Chim. Acta* **1996**, *318*, 175.
17. Menzel, E. R. *Anal. Chem.* **1989**, 557A-61A.
18. Crosby, G. A.; Whan, R. E.; Alire, R. M. *J. Chem. Phys.* **1961**, *34*, 744.
19. Sato, S.; Wada, M. *Bull. Japan Chem. Soc.* **1970**, *43*, 1955.
20. Mecartz, W. L.; Winefordner, J. D. *Anal. Chem.* **1966**, *38*, 848.
21. Horioctz, W. W.; Sudnick, W. *J. Am. Chem. Soc.* **1971**, *161*, 334.