Effects of Fluoroborates on the Visible Absorption Spectra of Lanthanum(III)-Alizarin Complexon Chelate[1]

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Recently, lanthanum(III) and cerium(III) chelates of alizarin complexon (ALC, 1,2-dihydroxyanthraquinone-3-yl-methylamine-*N,N'*-diacetic acid) have been widely utilized as a colorimetric reagent in trace analysis of fluorine since reported by Belcher *et al.*[2] The effectiveness and interesting behavior of the chelates have been described.[3] However, it has been reported that some anions and cations interfere with the determination of fluorine in the ALC method.[4]

We wish to report that, in the presence of potassium tetrafluoroborate (KBF_4) and one of its hydrolysis products, potassium monohydroxytrifluoroborate (KBF_3OH), the visible absorption spectrum of ALC-La chelate changes to that of ALC and this effect is especially remarkable in the presence of KBF_3OH.

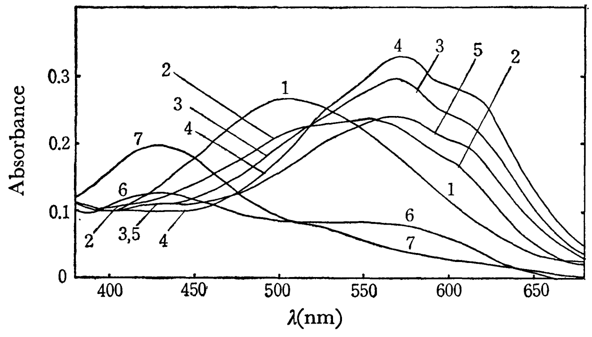

Fig. 1. Effect of KBF_4 on spectrum of ALC-La(III) chelate in acetic acid-sodium acetate buffer (pH 4.65) at 25°C. 1: 5×10^{-5}M ALC-La(allowed to stand for 90 min after adding ALC to $La(NO_3)_3$), 7: 5×10^{-5}M ALC. After adding 5×10^{-3}M KBF_4 to 1, 2: 1 min, 3: 5 min, 4: 11 hr, 5: 5 days, 6: 10 days.

As is shown in Fig. 1, in the presence of 100: 1 molar ratio of KBF_4 to ALC-La chelate, a peak of ALC-La chelate at 505 nm shifts to 572 nm and its spectrum nearly fits that of ALC-La-F ternary complex after 5 min. The spectrum gradually changes and a new peak corresponding to that of ALC appears at 428 nm after 10 days. The changes are accelerated with the rise of reaction temperature and KBF_4 concentration. Thus it is assumed that the effective species on these spectrum changes is not BF_4^- but one or more species of its hydrolysis products as described by the following equations.

$$BF_4^- + OH^- \rightleftharpoons BF_3OH^- + F^- \tag{1}$$

$$BF_3OH^- + OH^- \rightleftharpoons BF_2(OH)_2^- + F^- \tag{2}$$

$$BF_2(OH)_2^- + OH^- \rightleftharpoons BF(OH)_3^- + F^- \tag{3}$$

$$BF(OH)_3^- \rightleftharpoons B(OH)_3 + F^- \tag{4}$$

This is also supported by the results in Fig. 2. KBF_3OH is clearly more effective than KBF_4, that is, its spectrum quickly changes to that of ALC-La-F ternary complex at 20: 1 molar ratio of KBF_3OH to ALC-La chelate, and almost becomes that of ALC after 18.5 hr. The effect of KBF_3OH is also remarkable at 10: 1 molar ratio. It occurs in 40% acetone-water mixed solvent as well as aqueous solution.

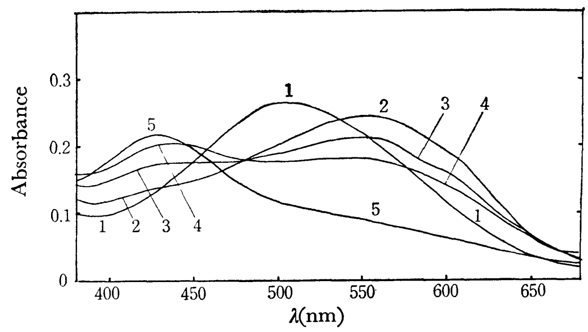

Fig. 2. Effect of KBF_3OH on spectrum of ALC-La(III) chelate in acetic acid-sodium acetate buffer (pH 4.65) at 25°C. 1: 5×10^{-5}M ALC-La(allowed to stand for 90 min after adding ALC to $La(NO_3)_3$). After adding 1.0×10^{-3}M KBF_3OH to 1, 2: 2 min, 3: 6 min, 4: 30 min, 5: 18.5 hr.

Thus we presume that the coexistence of boron has a considerable influence on the ALC method, and dissolved species of fluorine in the presence of boron and its behavior to ALC-La chelate become very important. In a previous paper,[5] we reported that the dissolved state of fluorine in sodium fluoride-boric acid-water system depended on the pH of the solution. The colorimetric determination of fluorine in the ALC method is usually carried out in the pH region 4.5—5. A considerable extent of fluorine in the sample solution is assumed to exist in fluoroborate forms in this region as described in Eqs. (1)—(3), unless boron is previously removed from the sample solution. Thus it seems that fluoroborates interfere with the formation of ALC-La-F ternary complex and are the cause of error in the determination of fluorine.

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1) Presented at 23rd Symposium of Analytical Chemistry, Tokushima, 5, June, 1971.

2) R. Belcher, M. A. Leonard, and T. S. West, *J. Chem. Soc.*, **1958**, 2390.

3) For example, I. Hosokawa, *Bunseki Kagaku*, **16**, 1259 (1967).

4) S. S. Yamamura, M. A. Wafe, and J. H. Sikes, *Anal. Chem.*, **34**, 1308 (1962).

5) Y. Moriguchi and I. Hosokawa, *Nippon Kagaku Zasshi*, **92**, 56 (1971).