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## The Direct Spectrophotometric Determination of Fluoride Ion

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## The Direct Spectrophotometric Determination of Fluoride Ion

GERALD F. BRUNZIE<sup>1</sup> AND RONALD T. PFLAUM<sup>1</sup>

*Abstract.* A direct method for the determination of fluoride ion in the parts per million range is described. The color reaction of fluoride ion and lanthanum chelate of 3-aminomethylalazarin-N,N-diacetic acid forms the basis for the spectrophotometric method. The intense blue fluoride complex in a mixed solvent system of 16% dimethylformamide-84% water is stable and independent of pH in the range of 4.6-5.6. Other halogens and common anions do not interfere in the measurements. Interfering ions are removed through ion exchange separations. Results on the determination of fluorine in selected samples are presented.

### INTRODUCTION

The search for a rapid and direct method for the quantitative determination of fluoride ion has occupied the attention of chemists since the time of Berzelius (6). Volumetric (10, 11, 20, 21), colorimetric (9, 18), nephelometric (19), and gravimetric (13, 14, 16) methods have been developed in addition to a number of spectrophotometric methods (7, 8, 12, 15). These methods require complicated procedures or time consuming distillations and careful control of variables. The presence of diverse ions often causes interference; phosphate, sulfate, and chloride ions being especially troublesome.

While alizarin derivatives have long been used in indirect colorimetric methods (20), the possibility of developing a direct

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method has only recently arisen. Belcher, Leonard, and West have used the blue color formed in the reaction of fluoride ion with the red cerium (III) chelate of 3-aminomethylalizarin-N, N-diacetic acid (alizerin complexone) for the qualitative detection (2) and for the quantitative determination of fluoride ion in organic compounds (3). Subsequent articles have dealt with a study of the color reaction (4) and with an evaluation of other lanthanons in the complex (5).

The present paper is concerned with the determination of fluorine in inorganic samples. A spectrophotometric study of the lanthanum complex in a mixed solvent system has been carried out. A study of the characteristics of this complex and its application in a proposed method of fluoride ion have been made.

#### EXPERIMENTAL

*Apparatus and Reagents.* All spectrophotometric measurements were made at 25°C with a Cary Model 11 recording spectrophotometer, using 1 cm. matched silica cells. All pH measurements were made with a Coleman Metrion pH meter.

Alizerin complexone, 3-aminomethylalizarin-N, N-diacetic acid, was obtained from the Hopkin and Williams Co., Ltd., Chadwell Heath, Essex, England. The acid was also synthesized in this laboratory, according to the procedure of Belcher, et al. (1), and a melting point of 178-180°C (lit. 178-180°C) was obtained.

A  $1.25 \times 10^{-2} M$  solution of lanthanum nitrate was prepared by dissolving 1.353 grams of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in 250 ml. of freshly distilled dimethylformamide (DMF) containing a few drops of nitric acid.

A reagent stock solution  $1 \times 10^{-2} M$  in lanthanum ion,  $2 \times 10^{-3} M$  in alizerin complexone (AC) and  $0.6 M$  in acetic acid-sodium acetate was prepared by dissolving 0.0722 grams ( $2 \times 10^{-4}$  moles) of the complexone in 80 ml. of the above lanthanum solution and diluting to 100 ml. with an acetate buffer. (The stock solution had a pH of 5.3 and was stable for a period of six months.)

A standard fluoride solution was prepared from certified grade sodium fluoride, obtained from the Fisher Scientific Co.

All other reagents were prepared from reagent grade chemicals and deionized water.

*The Color Reaction.* An absorptometric study of solutions of alizerin complexone (AC), various rare earth metal ions and AC, and rare earth metal ions, AC, and fluoride ion was carried out. Solutions  $2.40 \times 10^{-4} M$  in AC at various pH values were prepared by dissolving weighed amounts of the reagent in deionized water and adjusting the pH with dilute HCl and NaOH. Ultra-violet and visible absorption spectra were obtained from a

series of rare earth-AC solutions,  $2.40 \times 10^{-4} M$  in AC and  $2.40 \times 10^{-4} M$  in La(III), Ce(III), Nd(III), Pr(III), and Sm(III) ions. Equal amounts of fluoride ion were added to each solution to determine the most sensitive system.

The effects of variables in the lanthanum-alizarin complexone-fluoride ion system were determined in this study. The order of addition of the three components in the complex and the optimum concentrations of lanthanum ion, hydrogen ion and alizarin complexone, were evaluated. A time study of the rate of color formation was carried out. The effectiveness of acetone, acetonitrile, dimethylformamide, dioxane, ethanol, and methylcellosolve in preventing precipitation of the colored lanthanum species was ascertained.

The effects of diverse ions upon the color reaction were also determined in this investigation. Solutions were prepared containing 210 ppm of a salt of the ion, 2.1 ppm of fluoride ion, and 10 ppm of the lanthanum-complexone chelate. Absorptimetric data were used as a measure of the effect of the diverse ion. The absorption of the solutions (versus  $H_2O$ ) at  $623 m\mu$  was compared to that of a standard. Solutions having deviations exceeding 2% were considered to contain an interfering ion.

*Determination of Fluoride Ion.* Four synthetic solutions were prepared, one having a final concentration of 200 ppm each of ferric nitrate, cobalt chloride and nickel acetate and 1.10 ppm fluoride ion. The second contained 1.10 ppm fluoride ion in addition to 200 ppm concentrations of silver, mercury, and lead nitrate salts. These solutions were made by passing a solution of the components through a column containing IR 120 ion exchange resin, the effluent being collected in a 25 ml flask containing 5.00 ml of the reagent stock solution.

The other solutions, S-3 and S-4, contained phosphate and arsenate respectively, at a molar concentration three times that of fluoride (1.5 ppm F-present).

The NBS-91 opal glass sample (0.0938 grams) was prepared by fusing with approximately one gram of sodium carbonate in a platinum crucible. The mass was then dissolved in a small amount of deionized water and the resulting flocculent precipitate was filtered off. The filtrate was diluted to 250 ml and a one ml aliquot taken for analysis. Removal of the small amount of interfering substances remaining was effected by passing the aliquot through a column of a strongly acidic ion exchange resin (IR 120) and into a 25 ml flask containing 5.00 ml of the reagent.

*Recommended Procedure for Fluoride Ion.* After suitable preliminary treatment to affect dissolution of the sample, the re-

sultant sample solution is subjected to a separation procedure. Passage of the sample through a 1x12 cm. column of Dowex 50 or Rohm and Haas Amberlite IR 120 ion exchange resin in the sodium form removes interfering cations. Anions may be removed from the sample solution by passage through a similar column containing Dowex 1-x8. Fluoride ion is eluted out of the column with 0.2M sodium acetate solution (17).

Exactly 5.00 ml of the reagent stock solution is added to a 25 ml volumetric flask, followed by a suitable aliquot of the fluoride sample solution so as to give a final fluoride concentration of 0.1 to 2 ppm. The flask is brought to volume with deionized water and the absorbance of the solution at 623 m $\mu$ , versus a reference solution, is determined after waiting two hours for complete color development. The reference solution is prepared in the same manner as the fluoride sample solution, using deionized water in place of the sample. A calibration curve may also be prepared, using a standard sodium fluoride solution. The concentration of fluoride ion in the sample solution is calculated from the observed absorbances of the sample solution using the calibration curve.

RESULTS AND DISCUSSION

The absorption spectra of alizarin complexone solutions are

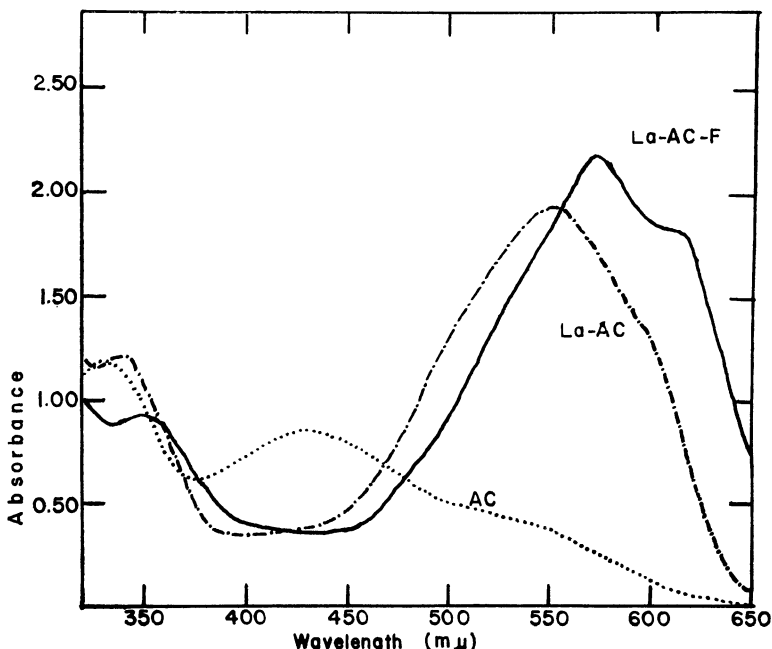


Figure 1. Absorption spectra of Ac, La-AC chelate, and La-AC-F complex; AC concentrations of  $2.40 \times 10^{-4}M$ , Lanthanum(III) concentrations of  $1.00 \times 10^{-3}M$  and excess fluoride ion; pH 5.3

dependent upon pH. Solutions of AC are yellow at pH 4, orange at pH 5.3, red at pH 9, and blue above pH 12. Solutions of the rare earth metal chelates are red at pH 5.3 and essentially independent of pH in the pH range 4.6 to 5.6. The addition of fluoride ion to a solution of the metal chelate results in a bathochromic shift in the absorption peak, causing the solution to become blue in color. The absorption spectra of AC, the La-AC chelate and the La-AC-F complex are shown in Figure 1. Experiments with cerium, neodymium, praseodymium, and samarium in place of lanthanum indicated that fluoride ion gives the most intense coloration with the lanthanum chelate of alizarin complexone.

Although the La-AC-F complex has an absorption maximum at  $570\text{ m}\mu$ , a differential spectrum obtained with an equivalent concentration of the lanthanum alizarin complexone chelate in the reference cell indicated an absorption maximum at  $623\text{ m}\mu$  (Figure 2). The absorbance at this wavelength was found to

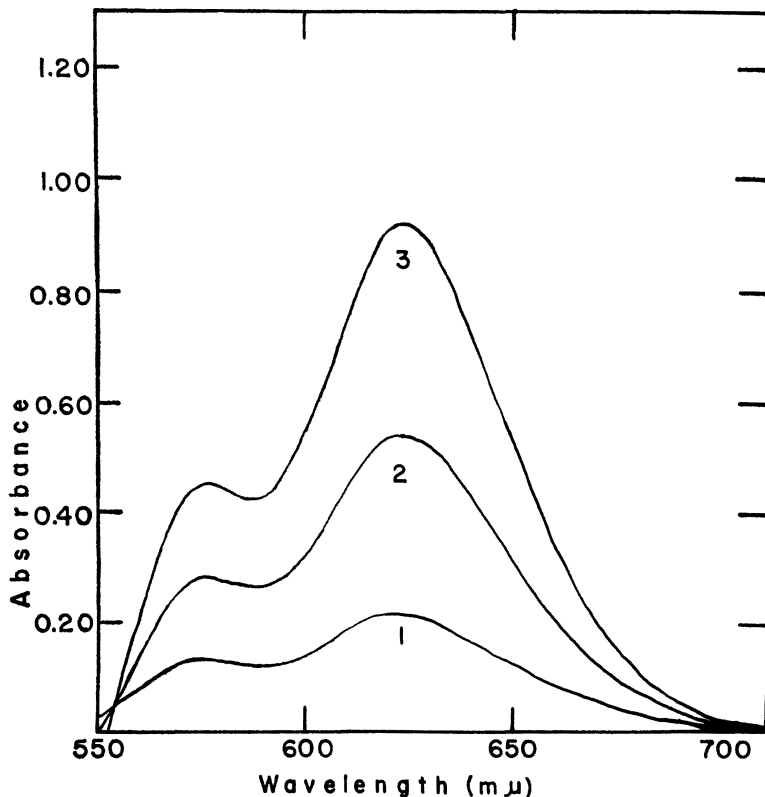


Figure 2. Effect of fluoride ion, vs. La-AC reference:

- 1)  $1.65 \times 10^{-5} M$  F<sup>-</sup>
- 2)  $4.20 \times 10^{-5} M$  F<sup>-</sup>
- 3)  $7.20 \times 10^{-5} M$  F<sup>-</sup>

be independent of pH in the range of 4.6-5.6. With a reagent concentration of  $4 \times 10^{-4} M$ , Beer's law is obeyed over a concentration range of 0.1-2.5 ppm of fluoride ion. Under the above conditions of measurement, the blue fluoride complex exhibits an apparent molar absorptivity of 12,790 at  $623 m\mu$  (based upon fluoride concentration).

While color development is initially more rapid if lanthanum ion is added to the solutions after fluoride ion, it was found that the time required for full development of the color is actually less when the fluoride is added to the La-AC chelate reagent.

The amounts of lanthanum and DMF present, relative to AC, do not influence the color reaction provided that at least a 1:1 ratio of La (III) to AC is used and that a minimum of 4 ml of DMF per 25 ml final volume is maintained. The use of La (III) ion in excess not only aids in complete chelation of complexone, but also prevents interference from a number of anions, such as citrate and tartrate, which would otherwise interfere.

*Effect of Diverse Ions.* Of the anions tested, only fluoride ion was found to form the characteristic blue color of the complex. Salts of the other halides have no effect on the intensity of the color, even when present at concentrations of 1050 p.p.m., or 500 times that of sodium fluoride. A La-AC-F solution containing 55000 p.p.m. sodium chloride was also free of interference. A number of monovalent anions cause interference: nitrite inhibits complete development of the blue color, vanadate prevents formation of any blue color, and high results were obtained with fluoroborate. Other interfering anions include phosphate, molybdate, tungstate, arsenate, oxalate, stannate, dichromate, fluoro-silicate, pyrophosphate, and sulfide. Oxalate and sulfide solutions were blue in color, but the solutions were found to contain precipitates. However, solutions having a 3 to 1 concentration ratio of phosphate or arsenate to fluoride were found to be free from interference. Except for  $BF_4^-$ , all interfering anions cause a decrease in absorbance.

Among the cations tested for interference, the alkali metals, Li, Na, K, and ammonium ion do not interfere, nor do the alkaline earth metals, Mg, Ca, Sr, and Ba. In addition, thallos, manganous, uranyl, and cadmium ions do not interfere.

The transition heavy metals, V(IV), Cr(III), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) interfere, preventing formation of any blue color. Pink or red-colored chelates form when Be(II), Al(III), Sn(II), Zr(IV), Bi(III), Ag(I), Hg(II), or Th(IV) are present. Although Belcher has indicated interference from iminodiacetic acid and citrate and tartrate salts (2), solutions of 210 ppm concentration did not interfere, due to the

formation of colorless complexes with excess lanthanum ion. Solutions containing cerous ion have slightly low absorbances and form precipitates within 24 hours.

Oxidizing substances also prevent formation of the blue complex. Addition of ceric ion yields colorless solutions. Permanganate ion discharges the color, leaving a brown precipitate. In the presence of silver ion, persulfate oxidizes the AC molecule, but by itself does not interfere, even when La-AC-F test solutions were allowed to stand overnight. Dichromate ion interferes, but does not oxidize the AC molecule. The presence of hydroxylamine, at a final concentration of 500 ppm  $(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$ , does not cause interference.

The use of ion exchange techniques in fluoride analysis has proven to be effective for the separation of interfering ions, and is especially useful for the removal of interfering cations(7). The method developed by Nielson(17), in which a strongly basic anion exchange resin is used to separate fluoride from phosphate ion, may be useful.

*Results on Selected Samples.* Solutions containing appreciable amounts of iron, cobalt, nickel or lead fail to develop any blue color upon the addition of fluoride ion. The presence of silver and mercuric ions do not completely prevent color formation, but cause interference. The results shown in Table I however, in-

**Table 1.** Results on Selected Samples

Sample	F <sup>-</sup> present, $\mu\text{g}$	F <sup>-</sup> found, $\mu\text{g}$	% error
S-1	27.5	26.1	-5.1
S-2	27.5	27.0	-1.8
S-3	37.5	37.5	0
S-4	37.5	38.2	+1.8
NBS 91	21.5	21.3	-0.77

dicate the feasibility of removal of interfering cations by ion exchange techniques.

Phosphate ion, especially troublesome in fluoride analysis, may be tolerated at molar concentrations 3 times as great as that of fluoride ion. Sample S-3,  $7.90 \times 10^{-5} M$  in fluoride, (1.50 p.p.m.) had a final phosphate concentration of  $2.37 \times 10^{-4} M$ .

In the treatment of the NBS-91 sample it was found that slightly low results (2½%) were obtained when the aliquot was not passed through the cation exchange column.

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## Anomalous Gas Exchange in Ascorbate Oxidation by the Myrothecium Enzyme

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*Abstract.* Manometric studies were employed to assay for ascorbic acid oxidase activity in cell free homogenates from the mycelium of the mold *Myrothecium verrucaria*. It was found that gas exchange measurements deviated from expected stoichiometry based on the utilization of one-half of a mole of oxygen for every mole of ascorbate oxidized. Oxygen was consumed in excess of the expected amount and carbon dioxide was produced during the course of the reaction. Apparently, the ascorbic acid oxidase reaction which produces dehydroascorbic acid is accompanied by or followed by other reactions involving oxygen consumption and carbon dioxide evolution.

### INTRODUCTION

Two enzymatic oxidations have been implicated in the transfer of electrons from ascorbic acid directly to oxygen. The first of these is by the well-characterized ascorbic acid oxidase from higher plants. This enzyme has been highly purified and the active site is known to be a copper prosthetic group. A second oxidase has been observed in lower plants. One of the characteristics of the latter is that heavy metal inhibitors do not block the oxidation of ascorbic acid. Primarily for this reason the lower plant oxidase has been termed "atypical."

Dunn and Dawson (4) showed that the stoichiometry of the purified ascorbic acid oxidase from higher plant sources involves the utilization of one-half of a mole of oxygen per mole

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