*New Colorimetric Determination of Small Quantities of Fluoride by Using p-Dimethylaminoazophenylarsonic Acid Zr Lake**

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A new colorimetric method for the determination of fluoride in low concentration by using *p*-dimethylaminoazophenylarsonic acid** Zr lake is based mainly on the following reaction :1)

$$\text{“Azodye”-Zr lake} + F^-(\text{or } SiF_6^{--}) \longrightarrow \text{“Azodye”} + \text{Zr-F complex ion.}$$

The liberated Azodye can be separated from the insoluble Zr lake by filtering and the absorbance of the red color of the “Azodye” solution is determined colorimetrically.

Reagent.—A series of standard sodium fluoride solutions containing 0.01 to 1.00 p.p.m. fluoride are to be prepared. Hydrochloric acid of 1 N, 2 N, and 6 N analytical grade.

Stock solution A: The "Azodye" solution is prepared by dissolving 0.2 g. of *p*-dimethylaminoazophenylarsonic acid in 100 ml. of 6 N HCl.

Stock solution B: The izrconyl chloride solution is prepared by dissolving 0.1 g. of $ZrOCl_2 \cdot 8H_2O$ in 100 ml. of 6 N HCl.

Preparation of Suspended Lake Reagent.—40 ml. of both stock solutions are mixed by dropping B into A gradually, and set for over 30 min. in room temperature. The insoluble reddish-brown lake obtained is centrifuged (at 3000 r.p.m. for a few min.), decanted, and washed with 2 N HCl repeatedly, and finally suspended in 200 ml. of 1 N HCl. This lake reagent is stable for several weeks in a dark place.

Procedure.—Ten ml. of sample solution (If the F^- concentration of sample is above 1 p.p.m., dilute it below 1 p.p.m.) and 10 ml. of standard fluoride solution are poured into matched test tubes with stoppers. Two ml. of 6 N HCl, and 1 ml. of suspended lake reagent are added to each tube, shaken for a few seconds and set for the same space of time strictly—e.g. for 1 hr.—at room temperature. (If more rapid determination is desired, it is possible to shorten this space of time.) Filter off the lake by filter paper (for quantitative use), and the colors of filtrates (being deeper according to F^- contents) are compared with each other, or the absorbancies of them are determined and compared, using a photoelectric colorimeter, spectrophotometer, or Duboscq colorimeter. The colored solution has an absorption maximum at 500 mμ. As the Beer's law conforms to these dye solutions in the above conditions (0—1 p.p.m. of F^-) it is easy and accurate to evaluate the F^- concentration of the sample solution using only three standard solutions when the colorimeter is used. The colored filtrates are so stable even when exposed to diffused sunlight for a long time that the absorbancy measurement need not be hasty.

Interfering substances which give ±0.05 p.p.m. error refering to 0—1 p.p.m. of F^- are: 2 p.p.m. of thiosulfate, sulfide, 5 p.p.m. of nitrite, cyanide, chromate, 10 p.p.m. of sulfite, permanganate, aluminum, 50 p.p.m. of sulfate, borate, antimony, tin, cadmium and iron. The other common substances do not interfere when their conc. are below 50 p.p.m. A large amount of organic substance interferes also considerably.

It is unnecessary to consider these substances in rain water, river water and ground water as usual. When a large amount of these substances is present, the separation of them from F^- is necessary.

Results.—The lowest concentration of the standard solution, whose color can be easily distinguished from that of the blank test using photoelectric colorimeter, is 0.01 p.p.m. of F^-.

Accuracy and reproducibility are satisfactory as follows: [Results obtained by using photoelectric colorimeter with 500 mμ. filter.]

	F^-(p.p.m.)	
	Present	Found
NaF solution	0.00	-0.00_5, -0.00_5, 0.01, 0.00, 0.00_5,
	0.50	0.49, 0.50, 0.50, 0.51, 0.50_5,
	1.00	1.00_5, 0.99, 1.00, 0.98_5, 1.02,
Sample A (rain water)		0.05_5, 0.06, 0.05_5, 0.06, 0.06,
Sample B (river water)		0.11_5, 0.11_5, 0.12, 0.11_5, 0.12_5,
Sample C (distillate of hot spring water distilled as H_2SiF_6)		0.89_5, 0.90_5, 0.89_5, 0.88_5, 0.90_5,

This rapid and simple method for the determination of the low concentration of fluoride can be widely applied to the determination of fluoride in natural waters.

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** Abbreviation: "Azodye"......*p*-dimethylaminoazophenylarsonic acid.

1) F. Feigl, and E. Rajmann, *Mikrochemie*, 12, 133 (1933).

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