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COMPARISON OF COLORIMETRIC FLUORIDE METHODS

By

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September 30, 1964

GENERAL ELECTRIC COMPANY
HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. AT(45-1)-1350 between the
Atomic Energy Commission and General Electric Company

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INTRODUCTION

Since fluoride ion badly corrodes some of the metal tubing in reactors, part-per-million fluoride levels in a variety of solid and liquid samples must be determined. Only colorimetric methods of analysis are sensitive to the amounts of fluoride available for determination.

Four recently reported colorimetric methods using the highly colored zirconium-SPADNS (ZrSp), thorium-SPADNS (ThSp), thorium-thoron (Thth), and lanthanum-alizarin complexone (LaAC) complexes for the determination of fluoride were compared to the zirconium-alizarin (ZrA) complex method now in common use. Sensitivity, precision, speed and the effect of some of the common interferences were determined for each of these methods.

SUMMARY

The LaAC method is more sensitive, faster, and more precise than the other methods tested and suffers from few interferences. The sensitivities of the methods in optical density units per μg of fluoride were ZrA - 0.101, ZrSp - 0.223, ThSp - 0.039, Thth - 0.034, and LaAC - 0.275. The ranges were ZrA - 0.30, ZrSp - 0.16, ThSp - 0.97, Thth - 0.88 and LaAC - 0.11 μg of fluoride. While the zirconium-alizarin method requires ninety minutes for color development and the lanthanum-alizarin complexone method requires twenty minutes, the other three required only five minutes. Metals interfere in all of the methods, but small amounts of neutralized nitric acid do not interfere in the zirconium-alizarine and lanthanum-alizarin complexone methods.

APPARATUS AND REAGENTS

A Beckman DU spectrophotometer with photomultiplier attachment and five centimeter cells was used for this study.
Alizarin Red S, Eastman Chemical #1051.
Zirconium-Alizarin indicator: Dissolve 0.184 g of $ZrO(NO_3)_2 \cdot H_2O$ in 29.4 ml of concentrated sulfuric acid and 150 ml of water. Dissolve 0.370 g of Alizarin Red S in water. Combine the two solutions and dilute to 1000 ml with water. Let stand one day before using.
SPADNS: 2-(p-sulfophenylazo)-1,8-dihydroxy-naphthalene-3,6-disulfonic acid, trisodium salt; Eastman Chemical #7309.
Zirconium-SPADNS indicator: Dissolve 0.161 g of $ZrOCl_2 \cdot 8H_2O$ in 300 ml of concentrated hydrochloric acid and dilute to 500 ml with water. Dissolve 3.75 g of SPADNS in 500 ml of water. Mix equal volumes of these two solutions. Maximum color development of this system takes several days, but the sensitivity toward fluoride is constant as soon as the zirconium and SPADNS are mixed.
Thorium-SPADNS indicator: Dissolve 0.022 g of $Th(NO_3)_4 \cdot 4H_2O$ in water. Dissolve 3.75 g of SPADNS in water. Mix the two solutions and dilute to 1000 ml.
Thoron: 2-(2hydroxy-3,6-disulfo-1-naphthylazo) benzene arsonic acid; Eastman Chemical #6748.

Thorium-thoron indicator: Solution A; dissolve 0.238 g of $Th(NO_3)_4 \cdot 4H_2O$ in 0.5N nitric acid and dilute to 100 ml with 0.5 N nitric acid. Solution B: dissolve 1.0 g of thoron in 1000 ml of water. Mix 1.0 ml of solution A, 10 ml of solution B, and 5 ml of perchloric acid and dilute to 100 ml with water.

Alizarin complexone: 1,2-dihydroxyanthraquinone-3-ylmethylamine-N,N-diacetic acid. This reagent is available from Hopkins and Williams Ltd., Chadwell Heath, Essex, England.

Lanthanum-alizarin complexone indicator: Dissolve 0.0479 g of alizarin complexone in 0.1 ml of concentrated ammonium hydroxide, 1 ml of 20 w% ammonium acetate and a few ml of distilled water. Filter the solution through Whatmann #1 filter paper. Wash the filter with a small volume of distilled water. Add 8.2 g of anhydrous sodium acetate and 6 ml of glacial acetic acid to the filtrate. Then add 100 ml of acetone slowly while swirling the container. Dissolve 0.0408 g of lanthanum oxide in 2.5 ml of 2 N hydrochloric acid, warming gently to aid dissolution. Mix these two solutions and dilute to 200 ml. Mix well and readjust the solution volume after about 30 minutes.

This reagent is stable for about a week.

Fluoride standard, 1 g/l: Dissolve in water 2.210 g of sodium fluoride which has been dried in an oven for 1 hour and dilute to 1000 ml.

Fluoride standard, 0.1 g/l: Dilute the 1 g/l standard with water as needed.

Iron, 1 g/l: Dissolve 0.100 g of electrolytic iron in hydrochloric acid and dilute to 100 ml with water.

Aluminum, 1 g/l: Dissolve 0.100 g of aluminum metal in 1 N hydrochloric acid and dilute to 100 ml with 1 N hydrochloric acid.

EXPERIMENTAL

Tests were prepared in 10.0 ml graduated cylinders with mixing by slow inversion of the cylinders five times. During the waiting period cylinders were allowed to stand on the bench top at room temperature. One, 5, and 10 µl of concentrated nitric acid, 10, 50, and 100 µl of 1 g/l iron and 5, 25, and 50 µl of 1 g/l aluminum were used for the interference studies.

Zirconium-alizarin; Prepare the standard curve with 0, 20, 50 and 75 µl of 0.1 g/l fluoride standard and interference studies with 50 µl of 0.1 g/l fluoride standard. Add 0.5 ml of indicator to each cylinder, dilute with water and mix. After 90 minutes read the optical densities at 520 mµ against a reference containing 100 µl of 0.1 g/l fluoride standard and 0.5 ml of indicator.

Zirconium-SPADNS: Prepare the standard curve with 0, 10, 20, and 30 µl of 0.1 g/l fluoride standard and interference studies with 20 µl of fluoride. Add 1.0 ml of indicator, dilute with water and mix. After 5 minutes read the optical densities at 590 mµ against a reference consisting of 700 µl of indicator diluted to 10 ml.

Thorium-SPADNS: Prepare the standard curve with 0, 20, 50, and 100 µl of 0.1 g/l fluoride standard and interference studies with 50 µl of fluoride. Add 1.0 ml of indicator, dilute with water and mix. After 5 minutes read the optical densities at 580 mµ against a reference consisting of 700 µl of indicator diluted to 10 ml.

Thorium-Thoron: Prepare the standard curve with 0, 50, 100 and 150 µl of 0.1 g/l fluoride standard and interference studies with 50 µl of fluoride. Add 2.0 ml of indicator, dilute with water and mix. After 5 minutes read the optical densities at 550 mµ against a reference consisting of 500 µl of 0.1 g/l fluoride standard and 2.0 ml of indicator diluted to 10 ml.

Lanthanaum-alizarin complexone: Prepare the standard curve with 0, 10, 20, and 50 µl of 0.1 g/l fluoride standard and interference studies with 20 µl of fluoride. Add 3 ml of indicator, dilute with water and mix. After 20 minutes read the optical densities at 622 mµ against one of the solutions which contains no fluoride.

DISCUSSION AND RESULTS

The basis of the ZrA, ZrSp, ThSp and Thth methods is the decomposition of the highly colored metal dye complex. When fluoride is added, it forms a more stable metal fluoride complex which is colorless. But when fluoride is added to the wine-red LaAC complex, the color is changed to lilac-blue. The absorption curves obtained are shown in Figure 1.

Both the LaAC and the ZrSp methods were more sensitive than the ZrA method, but the two thorium methods were less sensitive. Compared with 0.101 optical density unit per µg fluoride for the ZrA method, the LaAC method yielded 0.275 and the ZrSp method 0.223 units, while the ThSp and Thth methods yielded 0.039 and 0.034 units.

For all of the procedures, the range of optical density readings was about 0.030 units. Thus the error in µg of fluoride was greater for the less sensitive methods and it reached almost 1 µg for the least sensitive method.

The ZrA method took the longest time for maximum color development. It required ninety minutes while the LaAC method required twenty minutes, and the remaining three methods needed only five minutes.

Metals interferred in all of the methods. By forming more metal dye complex, metals present caused lower answers in the ZrA, ZrSp, ThSp, and Thth methods. In the LaAC method, 10 µg levels of metal present caused high answers while a greater amount of metal caused precipitation of the dye. If it was neutralized, nitric acid did not interfere in the ZrA method (up to 1 ml) or the LaAC method (up to 0.25 ml). Even if it was neutralized, nitric acid did interfere in the other three methods. The thorium-SPADNS method was very sensitive to free acid concentration; the metal-dye complex faded completely in the presence of any free acid. These results are summarized in Table 1.

TABLE 1

COMPARISON OF METHODS

Method	Sensitivity O.D. units/µg F	Range O.D. units	Range µg F	Speed Minutes	Interference µg F/µl HNO_3
ZrA	.101	.030	.30	90	none
ZrSp	.223	.035	.16	5	.035
ThSp	.039	.038	.97	5	.700
Thth	.034	.030	.88	5	.045
LaAC	.275	.030	.11	20	none

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