Colorimetric Determination of Fluoride in Commercial Samples of Sodium Monofluorophosphate

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In an investigation of the hydrolysis of the monofluorophosphate ion, a rapid method for the determination of fluoride in samples of impure sodium monofluorophosphate and its hydrolysis products was desired. Hill and Reynolds (1) determined fluoride in the presence of orthophosphate and monofluorophosphate by a modification of the Steiger and Merwin method (4). This method employs a complex of titanium and peroxide as the colorimetric reagent, but Hill and Reynolds found that an extrapolation procedure had to be used due to appreciable hydrolysis of the monofluorophosphate ion in the colorimetric reagent. Another method that has been used successfully by White (5) involves precipitation of monofluorophosphate as the silver salt from cold 80 per cent ethanol with subsequent determination of fluorine in the precipitate by distillation with sulfuric or perchloric acid, according to the procedure of Willard and Winter (6) as modified by Rowley and Churchill (3). Fluoride ion is calculated as the difference between the total fluorine and precipitated fluorine in the silver monofluorophosphate.

Colorimetric methods based upon the bleaching of various colored ferric complexes by the fluoride ion have been widely used for determination of free fluoride in the absence of interferences. Among the interferences, however, are orthophosphate and monofluorophosphate ions. Another interference likely to be present in commercial samples of sodium monofluorophosphate manufactured by fusion of sodium fluoride and sodium metaphosphate is unreacted sodium metaphosphate.

By removing the orthophosphate, metaphosphate, and monofluorophosphate interferences by precipitation with alcoholic silver nitrate, and by selecting a colorimetric reagent which is unaffected by the excess silver nitrate and ethanol, it was possible to analyze impure sodium monofluorophosphate samples for uncombined fluoride ion.

Accordingly, a procedure was developed whereby:

1. Interferences are removed by precipitation with alcoholic silver nitrate on a semi-micro scale.
2. Titration of the hazy alizarin end-point with thorium nitrate is avoided.
3. Time is saved in routine analyses.

APPARATUS

The AC model Fisher electrophotometer, equipped with a green filter number 525-B and cylindrical absorption cells having a light path of approximately 23 mm. was used. Other apparatus needed included:

Volumetric pipette, 1 ml.
Mohr pipette, 10 ml.
Volumetric flasks, 100 ml. and 50 ml.
Cooling bath at 0°C.
Test tubes, 12 x 75 mm.
Centrifuge for 12 x 75 mm. test tubes.
Stirring rods or nickel spatulas.

REAGENTS

The following reagents are used in this procedure:
Saturated solution of silver nitrate in 95% ethanol.
Phenol red indicator.
Alcoholic sodium hydroxide solution containing 10 g. NaOH in 500 ml. 95% ethanol.

Ferric salicylate ("Ferrisal") colorimetric reagent. Dissolve 2.74 g. salicylic acid in 1000 ml. 95% ethanol. Transfer to a 10 liter bottle. Add 3.76 g. $Fe(NO_3)_3 \cdot 6H_2O$. Make volume up to 9.5 liters. Add 50 ml. concentrated reagent grade nitric acid.

Standard fluoride solution containing 1.00 mg. fluoride per ml. of solution Weigh 2.210 g. pure NaF and dissolve to make 1 liter of solution.

PROCEDURE

PREPARATION OF CALIBRATION CURVE. Pipette into 50 ml. volumetric flasks, 10 ml. portions of stock "Ferrisal" solution. Add varying volumes of the standard sodium fluoride solution containing from 0 to 1 mg. fluoride ion. At least 5 or 6 points should be taken for the calibration curve Make these flasks up to volume with distilled water. Read the per cent transmission of these solutions against distilled water in the Fisher electrophotometer. Plot per cent transmission against milligrams of fluoride ion added. This plot is almost linear.

The above procedure may be repeated using 25 ml. portions of "Ferrisal" solution made up to 100 ml. for a calibration curve good up to 2.5 mg. fluoride.

ANALYTICAL PROCEDURE.

1. Dissolve a weighed sample of the impure sodium monofluorophosphate in distilled water so that the resulting solution is about 0.1 molar.
2. Pipette 1.00 ml. of sample solution into a 12 x 75 mm. test tube.
3. Add one drop of phenol red indicator.
4. Add alcoholic sodium hydroxide solution dropwise until purple.
5. Add 3 ml. saturated alcoholic silver nitrate solution from a Mohr pipette.
6. Mix thoroughly with stirring rod or nickel spatula. Reserve this uncontaminated stirring instrument for later use on this same sample.
7. Cool in ice bath for approximately 5 minutes.
8. Centrifuge for approximately 2 minutes.
9. Decant liquid directly into a prepared volumetric flask containing a pre-selected volume of "Ferrisal" solution which corresponds to the calibration curve being used.
10. Wash residue in test tube with 4 ml. of 80% ethanol solution. Break up the precipitate with the same end of stirring instrument that was used in step 6.
11. Cool as in step 7.
12. Centrifuge as in step 8.
13. Decant liquid directly into same volumetric flask as in step 9.
14. Repeat steps 10-13 until no more fluoride is recovered when washings are added to a fresh portion of "Ferrisal" solution.
15. Make colorimetric reagent up to volume with distilled water.
16. Determine the per cent transmission of this solution relative to distilled water.
17. Relate this per cent transmission to milligrams of fluoride using previously prepared calibration chart. Be sure to add to this value any fluoride which was found in step 14.

NOTES. (Numbers refer to steps 1-17 above.)

1. The concentration is automatically limited by the equivalent of silver nitrate added in step 5.
2. This size sample and test tube were found convenient because a small centrifuge could be used. There is no reason for believing, however, that the method could not be adapted to larger (or smaller) samples.

3-4. Adjustment of *p*H is necessary because the silver precipitate is soluble in acid solution.

5. Silver monofluorophosphate and silver orthophosphate precipitate white and yellow, respectively. Silver trimetaphosphate is white.

6. This mixing instrument retains a small amount of liquid which is recovered in step 10.

7. Three to five minutes cooling time gives reproducible results.

8-9. Any solid in the liquid would invalidate results because monofluorophosphate ions interfere with colorimetric reagent.

10-14. These steps recover fluoride not recovered in initial centrifugate. Larger amounts of fluoride require more washings than smaller quantities for complete recovery.

15-17. These steps put analysis on same basis as calibration curve.

EXPERIMENTAL

SELECTION OF COLORIMETRIC REAGENT. Among the ferric complexes which have been used for colorimetric reagents in fluoride analysis are acetylacetonate, thiocyanate, "Ferron" complex, 5-sulfosalicylate, and salicylate. Salicylate was chosen from the above list because of the solubility of its silver salt and because salicylic acid is available in very pure form. Greenspan and Stein (2) used the ferric-salicylate complex prepared from ferric chloride and salicylic acid.

Preliminary experimentation showed that a colorimetric reagent prepared from ferric nitrate and salicylic acid was bleached by fluoride ions, but was unaffected by moderate amounts of aqueous silver nitrate. Addition of alcoholic silver nitrate, however, produced a slight lowering of the per cent transmission readings. Further experimentation showed that when ethanol was already present, further addition of ethanol in moderate amounts had no effect on the per cent transmission values. A satisfactory colorimetric reagent, then, was the ferric-salicylate complex in 10 per cent ethanol solution.

ANALYTICAL RESULTS. The analytical procedure has been checked and found to give quantitative recovery of fluoride from prepared samples of Na_2PO_3F of known purity and pure NaF.

A representative commercial sample of sodium monofluorophosphate obtained from the Ozark-Mahoning Company, Tulsa, Oklahoma, contained 96.2% Na_2PO_3F and 2.15% NaF, as determined by the Ozark-Mahoning Company. Determination of the fluoride in this sample by the analytical procedure reported here, gave 2.18% NaF.

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