METHOD #: 340.1	Approved for NPDES and SDWA (Ed. Rev. 1974, 1978)
TITLE:	Fluoride, Total (Colorimetric, SPADNS with Bellack Distillation)
ANALYTE:	CAS # F Fluoride 7782-41-4
INSTRUMENTATION:	Spectrophotometer
STORET No.	Total 00951 Dissolved 00950

1.0 Scope and Application

1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method covers the range from 0.1 to about 1.4 mg/L F. This range may be extended to 1000 mg/L using the Fluoride Ion Selective Electrode Method (340.2) after distillation.

2.0 Summary of Method

2.1 Following distillation to remove interferences, the sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl- SPADNS dye is a function of the fluoride concentration.

3.0 Comments

3.1 The SPADNS reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 414:1, p 388, Standard Methods for the Examination of Waters and Wastewaters, 14th Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent addition is the most prominent source of error in this test.

3.2 Care must be taken to avoid overheating the flask above the level of the solution. This is done by maintaining an even flame entirely under the boiling flask.

4.0 Apparatus

4.1 Distillation apparatus: A 1-liter round-bottom, long-necked pyrex boiling flask, connecting tube, efficient condenser, thermometer adapter and thermometer reading to 200°C. All connections should be ground glass. Any apparatus equivalent to that shown in Figure 1 is acceptable.

4.2 Colorimeter: One of the following

4.2.1 Spectrophotometer for use at 570 nm providing a light path of at least 1 cm.

4.2.2 Filter photometer equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm and a light path of at least 1 cm.

5.0 Reagents

5.1 Sulfuric acid, H_2SO_4, conc.

5.2 Silver sulfate, Ag_2SO_4 crystals.

5.3 Stock fluoride solution: Dissolve 0.221 g anhydrous sodium fluoride, NaF, in distilled water in a l-liter volumetric flask and dilute to the mark with distilled water; 1.00 mL = 0.1 mg F.

5.4 Standard fluoride solution: Place 100 mL stock fluoride solution (5.3) in a 1 liter volumetric flask and dilute to the mark with distilled water; 1.00 mL = 0.010 mg F.

5.5 SPADNS solution: Dissolve 0.958 g SPADNS, sodium 2-(parasulfophenylazo)-1,8- dihydroxy-3,6-naphthalene disulfonate, in distilled water in a 500 mL volumetric flask and dilute to the mark. Stable indefinitely if protected from direct sunlight.

5.6 Zirconyl-acid reagent: Dissolve 0.133 g zirconyl chloride octahydrate, $ZrOCl_2 \bullet 8H_2O$ in approximately 25 mL distilled water in a 500 mL volumetric flask. Add 350 mL conc HCl and dilute to the mark with distilled water.

5.7 Acid-zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution (5.5) and zirconyl-acid reagent (5.6). The combined reagent is stable for at least 2 years.

5.8 Reference solution: Add 10 mL SPADNS solution (5.5) to 100 mL distilled water. Dilute 7 mL conc HCl to 10 mL and add to the dilute SPADNS solution. This solution is used for zeroing the spectrophotometer or photometer. It is stable and may be used indefinitely.

5.9 Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water (CAUTION: Toxic-avoid ingestion).

6.0 Procedure

6.1 Preliminary distillation

6.1.1 Place 400 mL distilled water in the distilling flask.

6.1.2 Carefully add 200 mL conc. H_2SO_4 and swirl until contents are homogeneous.

6.1.3 Add 25 to 35 glass beads, connect the apparatus (Figure 1 making sure all joints are tight.

6.1.4 Heat slowly at first, then as rapidly as the efficiency of the condenser will permit (distillate must be cool) until the temperature of the flask contents reaches exactly 180°C. Discard the distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillations.

6.1.5 Cool to 120°C or below.

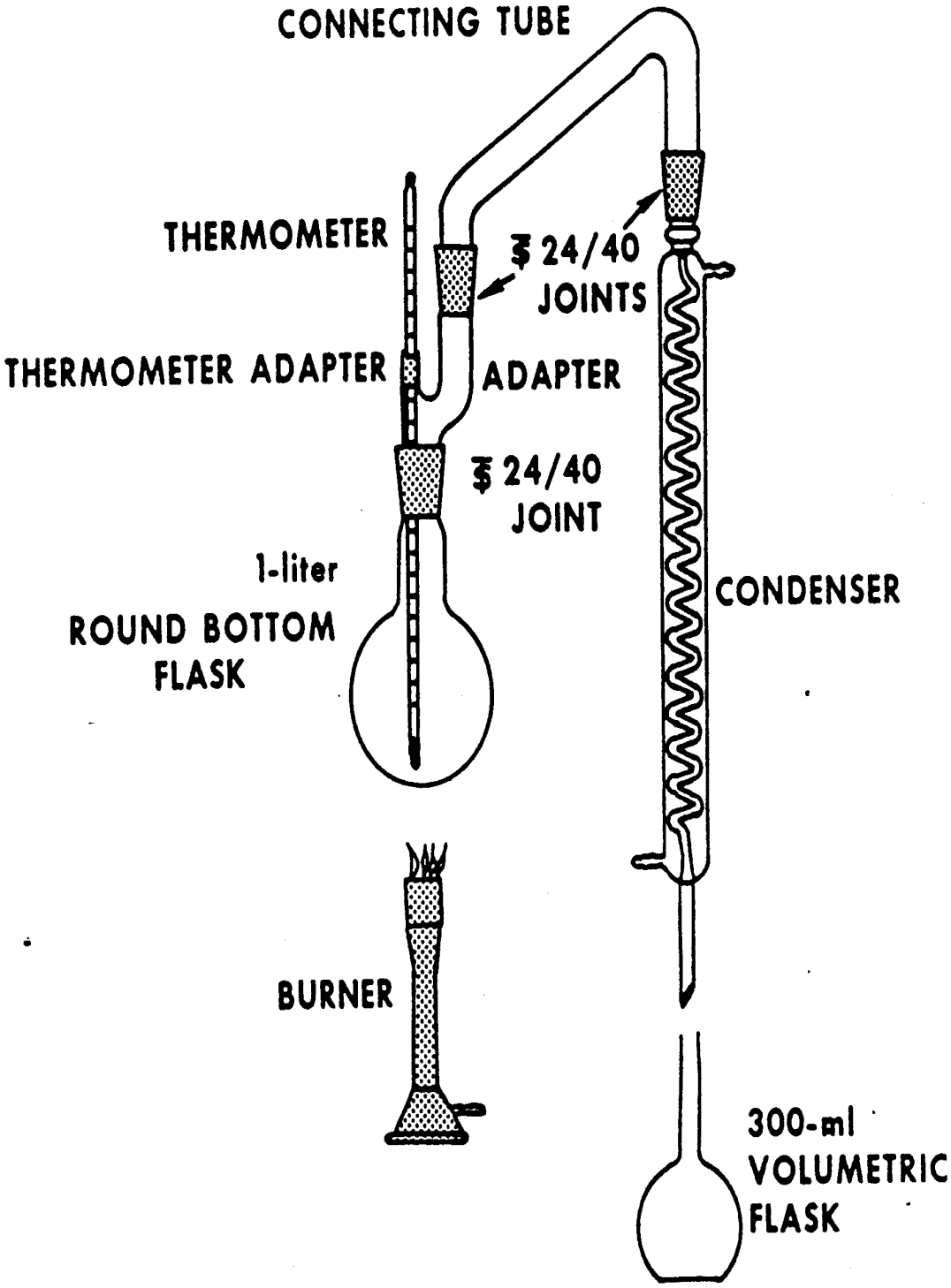

FIGURE 1 DIRECT DISTILLATION APPARATUS FOR FLUORIDE.

6.1.6 Add 300 mL sample, mix thoroughly, distill as in 6.1.4 until temperature reaches 180°C. Do not heat above 180°C to prevent sulfate carryover.

6.1.7 Add Ag_2SO_4 (5.2) at a rate of 5 mg/mg Cl when high chloride samples are distilled.

6.1.8 Use the sulfuric acid solution in the flask repeatedly until the contaminants from the samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check periodically by distilling standard fluoride samples.

6.1.9 High fluoride samples may require that the still be flushed by using distilled water and combining distillates.

6.2 Colorimetric Determination

6.2.1 Prepare fluoride standards in the range 0 to 1.40 mg/L by diluting appropriate quantities of standard fluoride solution (5.4) to 50 mL with distilled water.

6.2.2 Pipet 5.00 mL each of SPADNS solution (5.5) and zirconyl-acid reagent (5.6) or 10.00 mL of the mixed acid-zirconyl-SPADNS reagent (5.7) to each standard and mix well.

6.2.3 Set photometer to zero with reference solution (5.8) and immediately obtain absorbance readings of standards.

6.2.4 Plot absorbance versus concentration. Prepare a new standard curve whenever fresh reagent is made.

6.2.5 If residual chlorine is present pretreat the sample with 1 drop (0.05 ml) $NaAsO_2$, solution (5.9) per 0.1 mg residual chlorine mix. Sodium arsenite concentrations of 1300 mg/L produce an of 0.1 mg/L at 1.0 mg/L F.

6.2.6 Use a 50 mL sample or a portion diluted to 50 mL. Adjust the temperature of the sample to that used for the standard curve.

6.2.7 Perform step 6.2.2 and 6.2.3.

7.0 Calculations

7.1 Read the concentration in the 50 mL sample using the standard curve (6.2.4)

7.2 Calculate as follows:

$$\text{mg/L F} = \frac{\text{mg F} \times 1{,}000}{\text{mL sample}}$$

7.3 When a sample (mL sample) is diluted to a volume (B) and then a portion (C) is analyzed, use:

$$\text{mg/L F} = \frac{\text{mg F} \times 1{,}000}{\text{mL sample}} \times \frac{B}{C}$$

8.0 Precision and Accuracy

8.1 On a sample containing 0.83 mg/L F with no interferences, 53 analysts using the Bellack distillation and the SPADNS reagent obtained a mean of 0.81 mg/L F with a standard deviation of ±0.089 mg/L.

8.2 On a sample containing 0.57 mg/L F (with 200 mg/L SO_4 and 10 mg/L Al as interferences) 53 analysts using the Bellack distillation obtained a mean of 0.60 mg/L F with a standard deviation of ±0.103 mg/L.

8.3 On a sample containing 0.68 mg/L F (with 200 mg/L SO_4, 2 mg/L Al and 2.5 mg/L [$Na(PO_3)_6$] as interferences), 53 analysts using the Bellack distillation obtained a mean of 0.72 mg/L F with a standard deviation of ±0.092 mg/L. (Analytical Reference Service, Sample 11 I-B water, Fluoride, August, 1961.)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, p. 389-390 (Method No.414A, Preliminary Distillation Step) and p. 393-394 (Method 414C SPADNS) 14th Edition, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1179-72, Method A, p. 310 (1976).