

METHOD #: 340.3

Approved for NPDES (Issued 1971)

TITLE:

Fluoride (Colorimetric, Automated Complexone)

ANALYTE:

CAS # F Fluoride 7782-41-4

INSTRUMENTATION:

Autoanalyzer

STORET No.

Total 00951

Dissolved 00950

1.0 Scope and Application

- 1.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes. The applicable range of the method is 0.05 to 1.5 mg F/L. Twelve samples per hour can be analyzed.
- 1.2 For Total or Total Dissolved Fluoride, the Bellack Distillation must be performed on the samples prior to analysis by the complexone method.

2.0 Summary of Method

- 2.1 Fluoride ion reacts with the red cerous chelate of alizarin complexone. It is unlike other fluoride procedures in that a positive color is developed as contrasted to a bleaching action in previous methods.

3.0 Sample Handling and Preservation

- 3.1 No special requirements.

4.0 Interferences

- 4.1 Method is free from most anionic and cationic interferences, except aluminum, which forms an extremely stable fluoro compound, AlF_6^{-3} . This is overcome by treatment with 8-hydroxyquinoline to complex the aluminum and by subsequent extraction with chloroform. At aluminum levels below 0.2 mg/L, the extraction procedure is not required.

5.0 Apparatus

- 5.1 Technicon AutoAnalyzer Unit consisting of:
 - 5.1.1 Sampler I.
 - 5.1.2 Manifold.
 - 5.1.3 Proportioning pump.
 - 5.1.4 Continuous filter.
 - 5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 650 filters.
 - 5.1.6 Recorder equipped with range expander.

6.0 Reagents

- 6.1 Sodium acetate solution: Dissolve 272 g (2 moles) of sodium acetate in distilled water and dilute to 1 liter.
- 6.2 Acetic acid-8-hydroxyquinoline solution: Dissolve 6 g of 8-hydroxyquinoline in 34 mL of conc. acetic acid, and dilute to 1 liter with distilled water.
- 6.3 Chloroform: Analytical reagent grade.
- 6.4 Ammonium acetate solution (6.7%): Dissolve 67 g of ammonium acetate in distilled water and dilute to 1 liter.
- 6.5 Hydrochloric acid (2 N): Dilute 172 mL of conc. HCl to 1 liter
- 6.6 Lanthanum alizarin fluoride blue solution⁽¹⁾: Dissolve 0.18 g of alizarin fluoride blue in a solution containing 0.5 mL of conc. ammonium hydroxide and 15 mL of 6.7% ammonium acetate (6.4). Add a solution that contains 41 g of anhydrous sodium carbonate and 70 mL of glacial acetic acid in 300 mL of distilled water. Add 250 mL of acetone. Dissolve 0.2 g of lanthanum oxide in 12.5 mL of 2 N hydrochloric acid (6.5) and mix with above solution. Dilute to 1 liter.
- 6.7 Stock solution: Dissolve 2.210 g of sodium fluoride in 100 mL of distilled water and dilute to 1 liter in a volumetric flask. 1.0 mL = 1.0 mg F.
- 6.8 Standard Solution: Dilute 10.0 mL of stock solution to 1 liter in a volumetric flask. 1.0 mL = 0.01 mg F.
 - 6.8.1 Using standard solution, prepare the following standards in 100 mL volumetric flask:

mg F/L	mL Standard Solution/100 mL
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.20	12.0
1.50	15.0

7.0 Procedure

- 7.1 Set up manifold as shown in Figure 1.
- 7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.
- 7.3 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.
- 7.4 Arrange fluoride standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples.
- 7.5 Switch sample line from distilled water to Sampler and begin analysis.

8.0 Calculation

- 8.1 Prepare standard curve by plotting peak heights of processed fluoride standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.
- 9.0 Precision and Accuracy
- 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 0.06, 0.15, and 1.08 mg F/L, the standard deviation was ± 0.018 .
- 9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.14 and 1.25 mg F/L, recoveries were 89% and 102%, respectively.

Bibliography

1. J.T. Baker Laboratory Chemical No. J 112 or equivalent.
2. Greenhaigh, R., and Riley, J. P., "The Determination of Fluorides in Natural Waters, with Particular Reference to Sea Water". Anal. Chim. Acta, 25, 179 (1961).
3. Chan, K. M., and Riley, J. P., "The Automatic Determination of Fluoride in Sea Water and Other Natural Water". Anal. Chim. Acta, 35, 365 (1966).
4. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 614, Method 603, (1975).

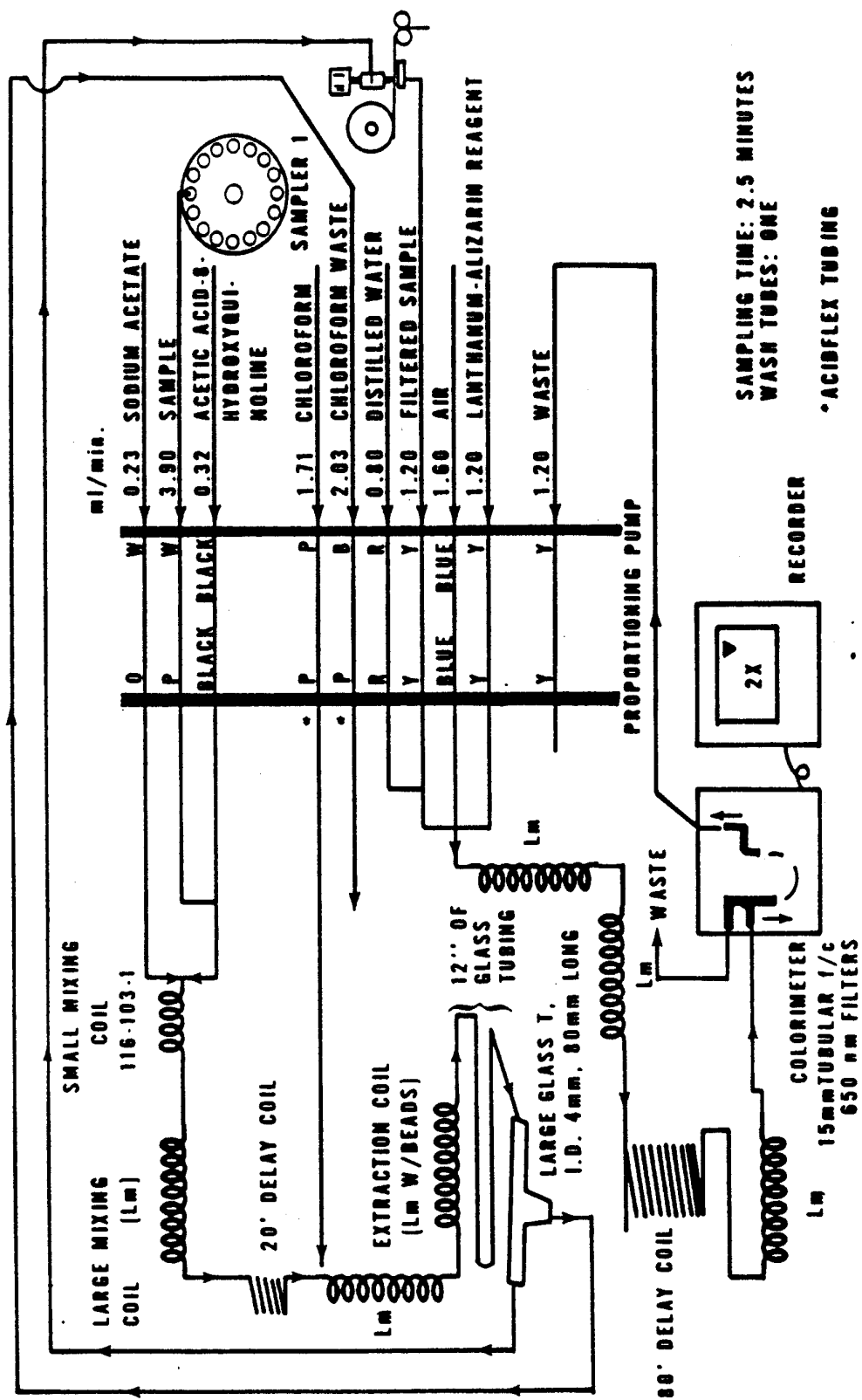


FIGURE 1. FLUORIDE MANIFOLD AA-1